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APPLICATION OF SURFACE CHEMICAL PRINCIPLES TO PITCH PROBLEMS

PART TWO: THE COLLOIDAL STABILITY OF PITCH FROM KRAFT AND GROUNDWOOD PULPS

Project 3317

Report Two

A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

May 15, 1979

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PART TWO: THE COLLOIDAL STABILITY OF PITCH FROM KRAFT AND GROUNDWOOD PULPS

SUMMARY

In pursuing studies concerned with the surface chemical behavior of pitch, an examination was made of the stability of colloidal pitch isolated from unbleached softwood kraft (250 mL CSF) and hardwood groundwood pulps. Colloidal stability was determined by counting the number of pitch particles in a small but known volume of pulp filtrate with a microscope and hemacytometer. Stability measurements were made as a function of time with and without the addition of aluminum sulfate at pH 4 and calcium sulfate at pH 7.

The stability of colloidal pitch from the kraft, groundwood, and the previously tested sulfite pulp was also examined after concentrating in the absence of added salts. Finally, colloidal stability was determined under high shear conditions. As a supplement to this work, pulp and water samples drawn from a kraft mill system were examined under the microscope for the presence of flocculent materials.

The tendency for pitch in matrix form to collect on stainless steel surfaces was studied in several series of microdeposit tests. The deposit tests with kraft pulp were carried out over a range of conditions with respect to pitch concentration, pH, time, temperature, and rate of agitation. The effects of pitch dispersant and added fiber were also examined. Tests with groundwood pitch were limited to the effects of pH, rate of agitation, and the addition of dispersant or fiber. Chemical analyses were made of pitch in matrix form from both pulps and of deposited pitch from the kraft pulp.

Results of this study indicate that isolated colloidal pitch from the kraft and groundwood pulps is stable with respect to time although the kraft pitch was found to be the least stable of the three pulps tested thus far in the program. The results further indicate that matrix floc networks with trapped pitch particles are formed by concentrating the isolated pitch suspensions as well as by the addition of aluminum sulfate at pH 4 or calcium sulfate at pH 7. The concentration left in suspension after addition of 100 mg/L of aluminum sulfate or 344 mg/L of calcium sulfate was reduced to less than one-half the original concentration within 12-48 hours. Generally speaking, the flocs produced from the groundwood pulp were smaller and less distinct than those from kraft, particularly in the presence of the calcium salt. Subjecting the isolated pitch suspension to high shear conditions failed to produce a significant shift in particle count or particle size distribution. Examination of samples drawn from a kraft mill system revealed the presence of flocculent material in the headbox and tray water. A relatively low number of trapped pitch particles were evident in these flocs due apparently to a low concentration of colloidal pitch beyond the brown stock washers. Nevertheless, the flocs present in the mill system resembled those produced in the laboratory in the presence of fiber and aluminum sulfate.

Microdeposition data indicated a difference in the tendency for kraft and groundwood pitch in matrix form to deposit on stainless steel surfaces depending upon the conditions employed. In the case of kraft pitch, deposition increased with increase in concentration, temperature, and time and rate of agitation. Deposit level declined with increase in pH and with addition of dispersant (sodium naphthalene sulfonate) or fiber. In contrast, deposit levels from groundwood matrix pitch reached a maximum at an intermediate rate of agitation (1800 rpm) and at a pH of 8 followed by a dramatic decline with increasing rpm or pH. Addition of fiber produced irregular behavior in deposit level. Photomicrographs revealed that fiber added to matrix pitch becomes attached to the floc network and, in some cases, fiber fragments appear to be imbedded in the floc. As was found in the case of kraft pitch, increases in the amount of dispersant decreased groundwood pitch deposit levels. Zeta potentials measured in the presence of aluminum sulfate (matrix floc conditions) were found to depend on pH but a consistent relationship between zeta potential and deposit level was not indicated.

The material deposited on stainless steel was found to be only partly comprised of pitch as indicated by the solubility in benzene-alcohol. Chemical analysis showed that pitch in matrix form contained carbohydrate and metal components in addition to the solvent-soluble material. The analysis further indicated that the total carbohydrate content of the matrix flocs remained reasonably constant as did the cellulose:hemicellulose ratio in the presence of aluminum sulfate. Ash and metal contents varied considerably depending upon the ionic environment. A composite of material deposited from kraft pitch on stainless steel was found to contain the same components as the isolated matrix pitch although some differences were indicated in the proportions of the components.

In brief summation, pitch in matrix floc form has been found to develop when colloidally suspended pitch from the unbleached kraft, sulfite, and groundwood pulps is concentrated in the absence of added salts as well as under more dilute conditions in the presence of aluminum and calcium salts. In addition to pitch, the matrix flocs have been found to contain cellulose, hemicellulose, and inorganic components depending upon the ionic environment. The results of this study also showed that pitch deposited on stainless steel in the presence of aluminum sulfate was comprised of the same components as the floc network.

Thus no evidence has been found in this phase of the experimental program to indicate that colloidally suspended pitch particles agglomerate to form the nucleus of pitch balls. Rather, considerable evidence has been produced which indicates that individual pitch particles become trapped in matrixlike flocs resulting from the destabilization of protective colloids. Conceivably these bulky flocs become attached to one another to form macroscopic particles capable of plugging papermaking wires and felts. While agglomeration of individual pitch particles may occur in the absence of protective colloids, this condition is believed to be the exception rather than the rule since it would seem reasonable to expect that most pulp and papermaking systems contain some measure of protective colloids in the form of hemicellulose, finely divided cellulose, starch, gums, etc. Destabilization of colloidal pitch via matrix floc formation finds some support in the fact that pitch deposits found in practical mill systems are rarely comprised solely of pitch but generally contain hydrous materials and metals as found in the matrix flocs. This does not necessarily apply to pitch deposited on shear surfaces or upon collapse of surface films.

INTRODUCTION

This is Progress Report Two on Project 3317 entitled "Application of Surface Chemical Principles to Pitch Problems. Part Two: The Colloidal Stability of Pitch from Kraft and Groundwood Pulps."

Work described in Report One was directed at the colloidal stability of pitch from an unbeaten spruce sulfite pulp. This pulp, which is frequently considered troublesome from the standpoint of pitch problems, was found to contain an appreciable concentration of colloidally suspended pitch particles as determined by a manual counting procedure and by nephelometry. A depositable pitch test confirmed the potentially troublesome nature of the pulp. Colloidal pitch isolated from this pulp was found to be stable over a pH range of 5-10 with a projected half-life of 5-7 months. The suspension was also found to be stable with respect to shear and heat. However, the colloidal system comprised of individual pitch particles suspended in a protective colloid was found to be destabilized in the presence of mono-, di-, and trivalent cations. The protective colloid containing cellulose and hemicellulose was precipitated under these conditions trapping individual pitch particles in the process. The result was a matrix-type of floc network with the protective colloid constituting the continuous phase and the individual pitch particles, a discontinuous phase. No substantial evidence for flocculation of individual pitch particles was found in this study. These results suggested the need for a modified hypothesis covering colloidal pitch stability and its troublesome nature. However, before a modified hypothesis could be formulated it was deemed necessary to confirm the presence of protective colloids and matrix-type floc networks in other papermaking pulps. Accordingly, additional pulps were procured and the stability of pitch in these systems was investigated.

EXPERIMENTAL

COLLOIDAL PITCH STABILITY DETERMINATIONS

Supplies of aspen unbleached stone groundwood and softwood unbleached kraft were procured in conjunction with continuing work concerned with colloidal pitch stability as described in Report One. The pulps utilized in this phase of the program were sampled at the deckers. The groundwood pulp was comprised essentially of 100% aspen; the kraft pulp contained 95.2% of mixed softwoods including approximately 10% of balsam fir. The remainder of the overall furnish was comprised of 4.8% mixed hardwoods, principally maple.

An exploratory set of experiments was conducted to establish relative levels of colloidal pitch in each pulp. Since kraft pulps have been indicated to contain relatively low levels of colloidal pitch (1), a portion of this pulp was beaten in a Valley beater to 250 mL CSF in order to expedite release of pitch held in ray cells and resin canals. All samples were dewatered to approximately 25% solids to facilitate storage. The dewatered pulps were stored at 40°F in the presence of formaldehyde. Colloidal pitch was isolated from the pulps according to the procedures given in Report One with perhaps some minor variations. By way of brief review, colloidal pitch samples were prepared by a repeated disintegration and filtration procedure wherein 5.3 g of pulp (o.d. basis) was soaked in 250 mL of distilled water followed by 30 seconds treatment in a Waring Blendor and then by coarse filtration on an 85-mm Buchner funnel. The filtrate from this operation was then used as the dispersion medium for a second 5.3 g sample of pulp which was subjected to another disintegration and filtration procedure in which the pulp was filtered in 125-mL aliquots through No. 4 Whatman filter paper followed by 25-mL aliquots through 5 μm Millipore.

Initial particle counts were made with a microscope and hemacytometer as described in Report One. An estimate of the percentage of particles considered to be pitch was made from the ratio of spherical/nonspherical particles. Depositable pitch from the whole pulp was determined according to the canister method (Appendix II in Report One). Results are recorded in Table I.

Particle counts were then made on additional samples of pitch isolated from the groundwood and beaten kraft pulps without pH adjustment. Particle counts on these samples were made as a function of aging over a period of time covering one month or longer. Results are recorded in Table II. Particle count-time relationships are presented in Fig. 1. Note: Subsequent work with the kraft pulp was limited to the beaten material.

A very limited study was made of the effects of aluminum and calcium sulfates to determine if floc networks develop as was found previously in the case of the Mitscherlich sulfite pulp. For this purpose, colloidal pitch isolated from both pulps was treated with 100 mg/L of aluminum sulfate at pH 4 or with 344 mg/L of calcium sulfate dihydrate at pH 7. A small amount of fiber was added in several cases to establish the effect of fiber on the floc network in a qualitative manner. Floc systems developed with addition of the salts and, as previously found, particle counts could not be made in the presence of the flocculent material. Hence, initial counts were made on untreated controls and on treated samples after aging 1-4 days in the absence of fiber. Results are presented in Table III and in Fig. 2 and 3.

Photomicrographs of flocculent materials formed in the presence of aluminum or calcium sulfate were prepared at 600X using an Olympus microscope equipped with Polaroid camera. Photomicrographs were also prepared in the presence of small amounts of fiber. Results are shown in Fig. 4-9.

TABLE I

COLLOIDAL PARTICLE CONCENTRATION IN SAMPLES
ISOLATED FROM GROUNDWOOD AND KRAFT PULPS

Pulp	Condition	pH	Pulp Consistency at Time of Isolation, %	Pitch Particles, particles/sq	Other Particles, particles/sq	Total Particles, particles/sq	% Particles Considered to be Pitch	Depositable Pitch, mg
Unbleached kraft (sampled at deckers)	Unbeaten	9.0	2.1	3.9 ± 1.2	2.5 ± 1.1	6.4 ± 1.2	61	--
Unbleached kraft (sampled at deckers)	Beaten to 250 mL CSF	8.1	2.1	14.3	4.3	18.6 ± 3.0	77	20.2
Unbleached groundwood (sampled at deckers)	Unbeaten	6.4	0.85	87.5	14.0	101.5 ± 18.5	86	23.1

TABLE II

THE COLLOIDAL STABILITY OF PITCH FROM
KRAFT AND GROUNDWOOD PULPS

Pulp	pH	Aging Time, days	Particle Concentration, particles/sq
Unbleached softwood kraft	8.1	1/24	20.1 ± 3.2
		5	18.0 ± 4.3
		15	17.4 ± 2.9
		29	12.6 ± 2.4
Aspen stone groundwood[a]	6.4	1/24	201 ± 38
		5	205 ± 24
		12	215 ± 32
		22	195 ± 41
		36	206 ± 58

[a]Isolated at 2.1% pulp consistency. The pitch suspension was then diluted 10:1 to make the particle count. Particle counts were corrected to 2.1% consistency.

TABLE III

THE EFFECT OF IONIC ENVIRONMENT ON THE COLLOIDAL
STABILITY OF PITCH FROM GROUNDWOOD AND KRAFT PULPS

Pulp	Additives	pH	Aging Time, hr	Particle Count, particles/sq
Unbl. softwood kraft	None (control)	8.1	1	20.1 ± 3.2
	Alum, 100 mg/L	4.0	24	None
	$CaSO_4$, 344 mg/L	7.0	24	3.1 ± 0.13
Aspen stone groundwood	None (control)	6.4	1	201 ± 38
	Alum, 100 mg/L	4.0	24	50 ± 11
			48	46 ± 13
	$CaSO_4$, 344 mg/L	7.0	24	124 ± 25
			96	58 ± 14

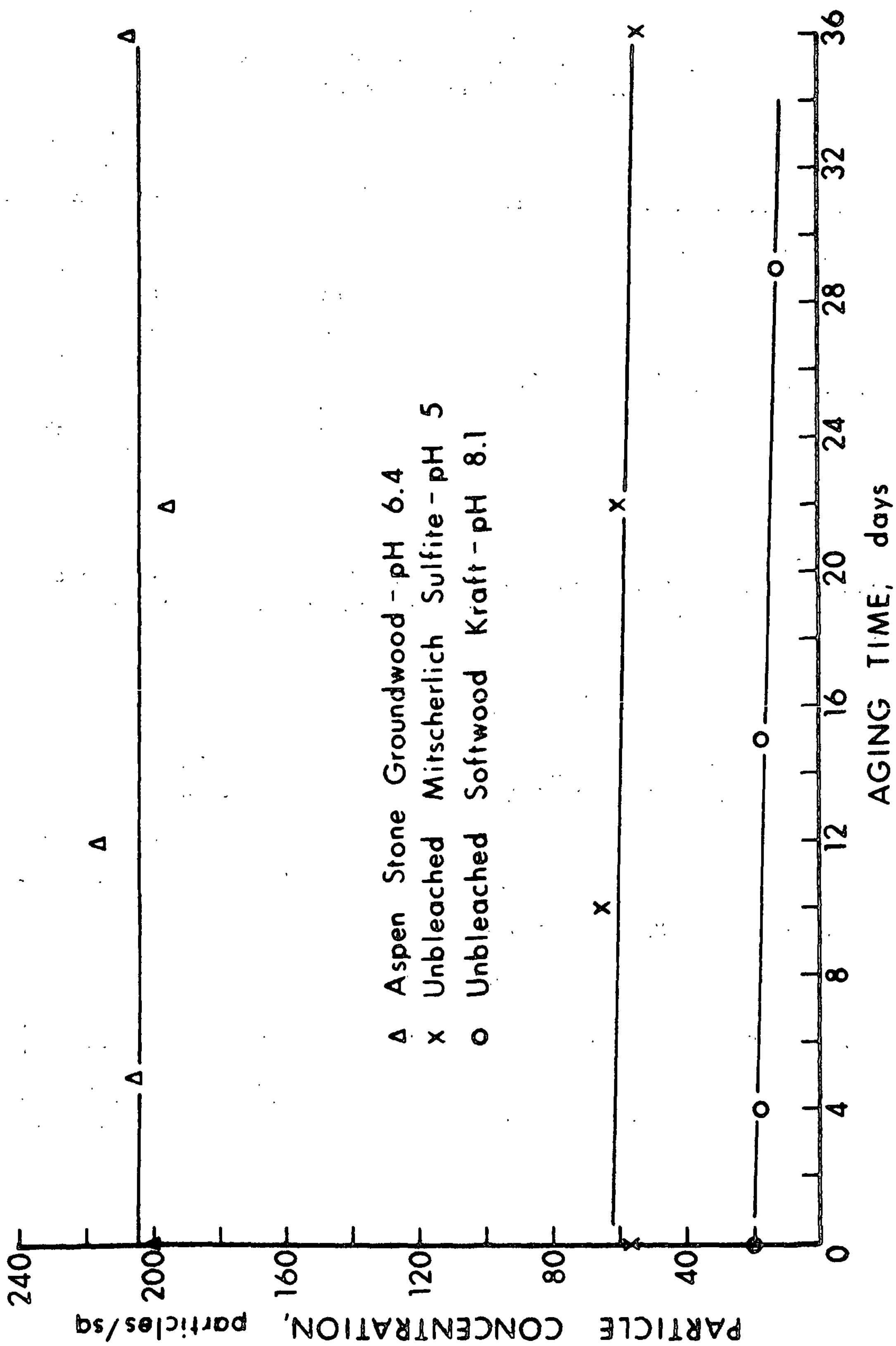

Figure 1. The Effect of Aging Time on the Colloidal Stability of Pitch

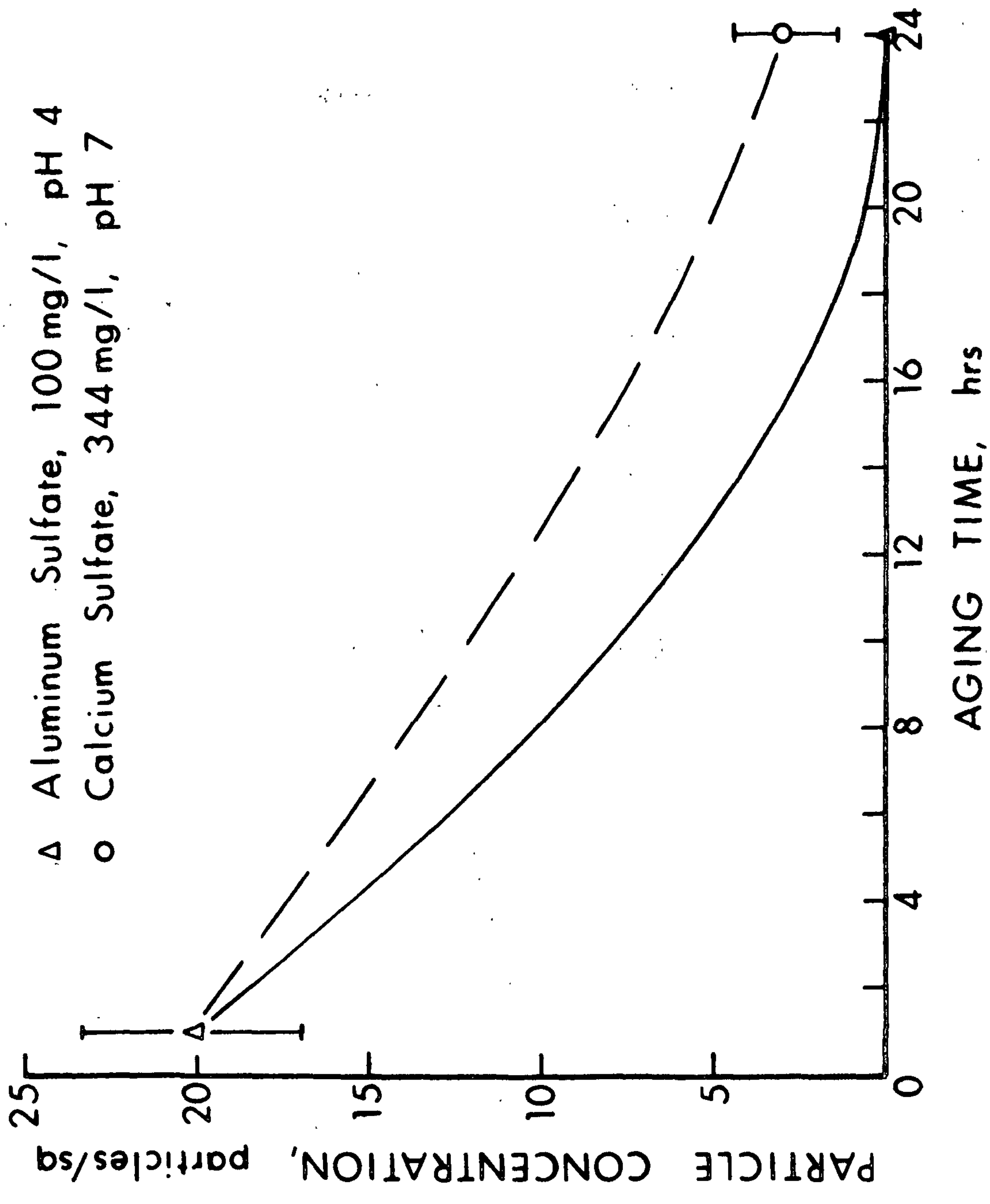

Figure 2. The Stability of Colloidal Pitch Suspensions from Unbleached Kraft Pulp in the Presence of Electrolytes

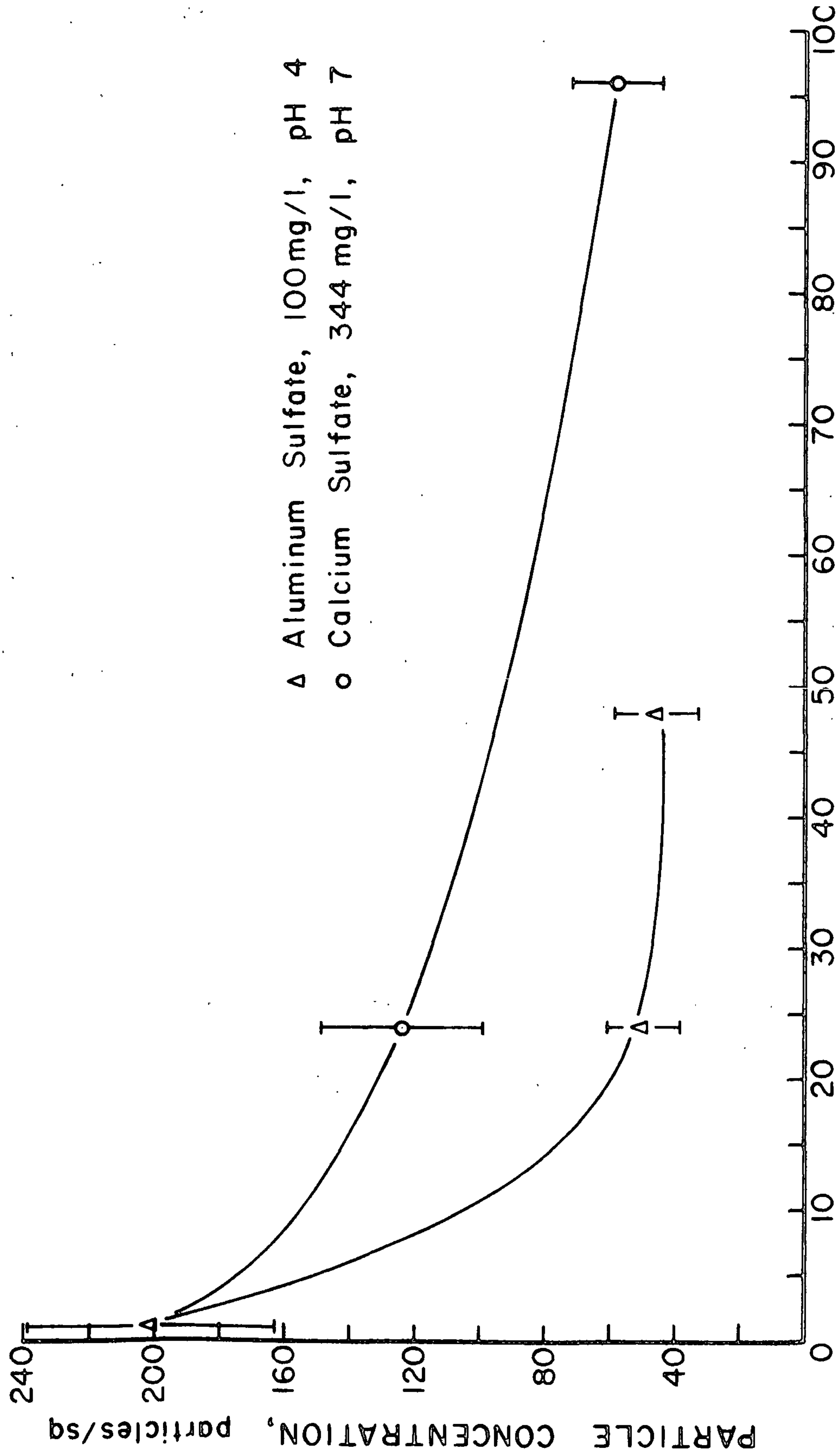

Figure 3. The Stability of Colloidal Pitch Suspensions from Unbleached Stone Groundwood in the Presence of Electrolytes

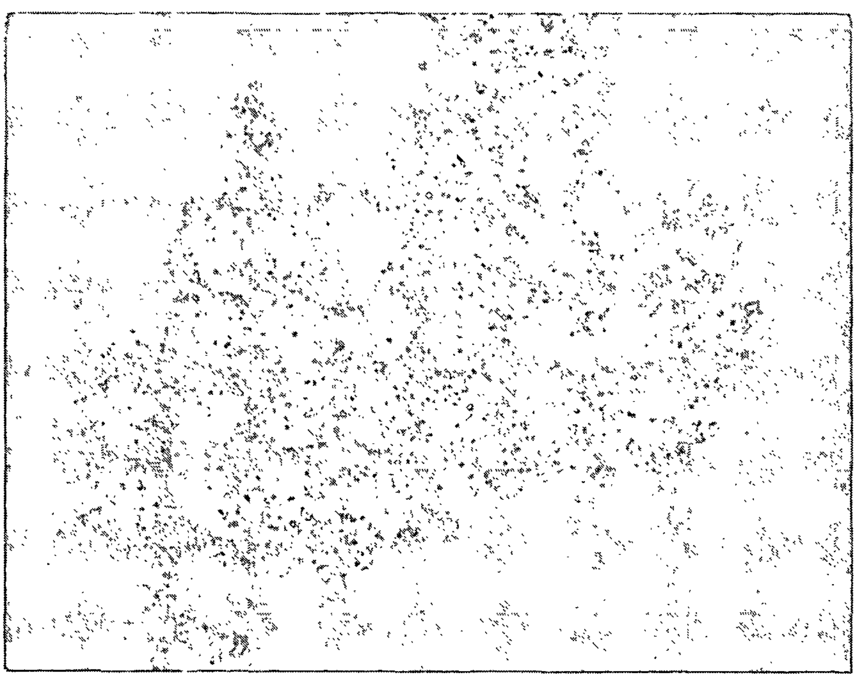

Figure 4. Flocculent Material Formed from Softwood Unbleached Kraft Pitch, 100 mg/L $Al_2(SO_4)_3$ Added at pH 4. 600X

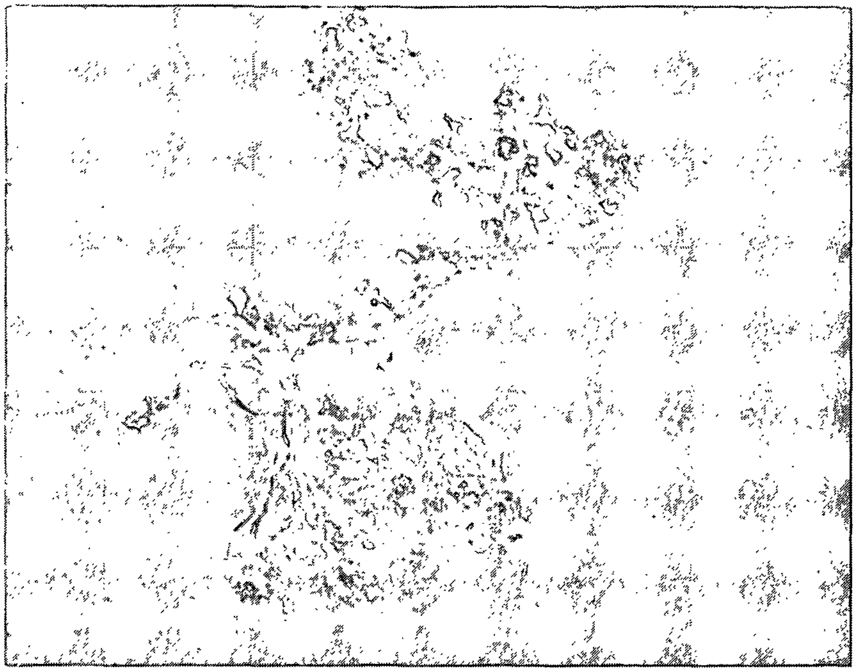

Figure 5. Flocculent Material Formed from Softwood Unbleached Kraft Pitch; Small Amount of Fiber + 100 mg/L $Al_2(SO_4)_3$ Added at pH 4. 600X

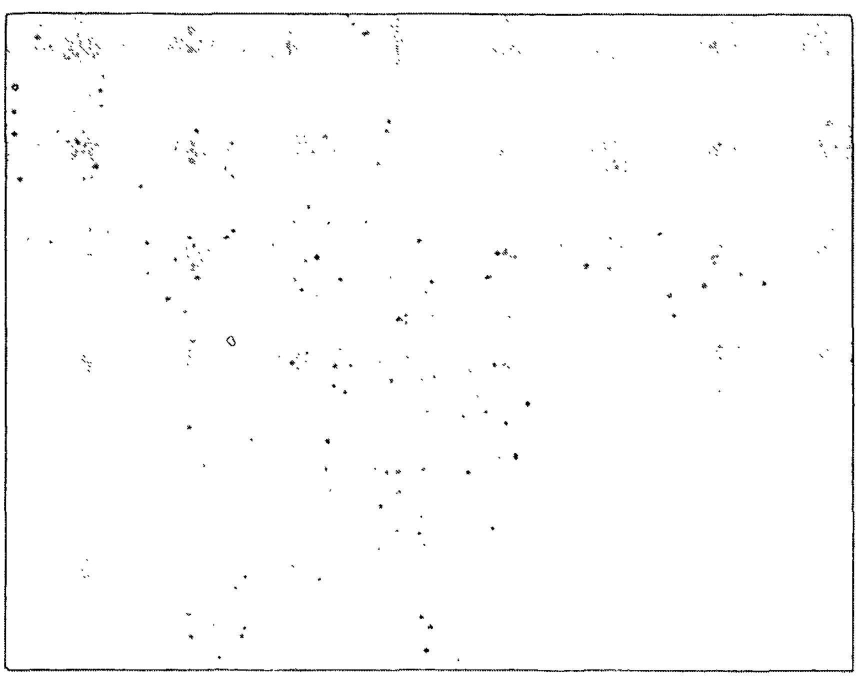

Figure 6. Flocculent Material Formed from Softwood Unbleached Kraft Pitch, 344 mg/L $CaSO_4$ Added at pH 7. 600X

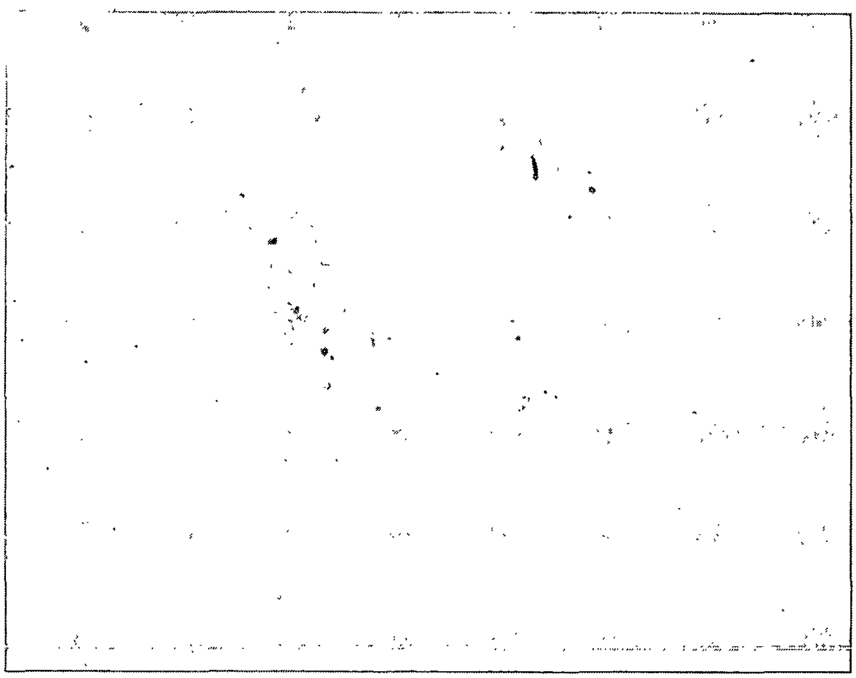

Figure 7. Flocculent Material Formed from Softwood Unbleached Kraft Pitch; Small Amount of Fiber + 344 mg/L of $CaSO_4$ Added at pH 7. 600X

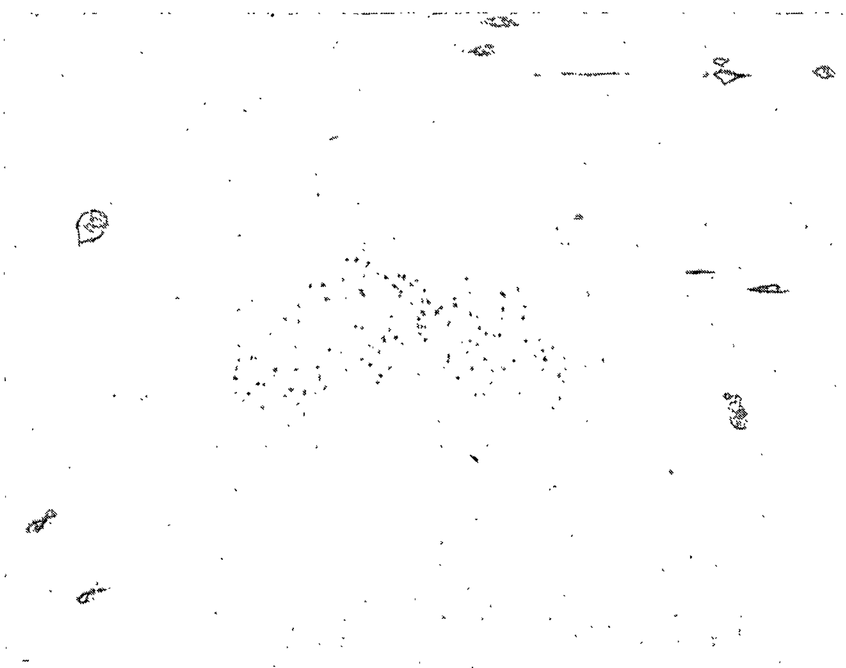

Figure 8. Flocculent Material Formed from Hardwood Groundwood Pitch, 100 mg/L $Al_2(SO_4)_3$ Added at pH 4. 600X

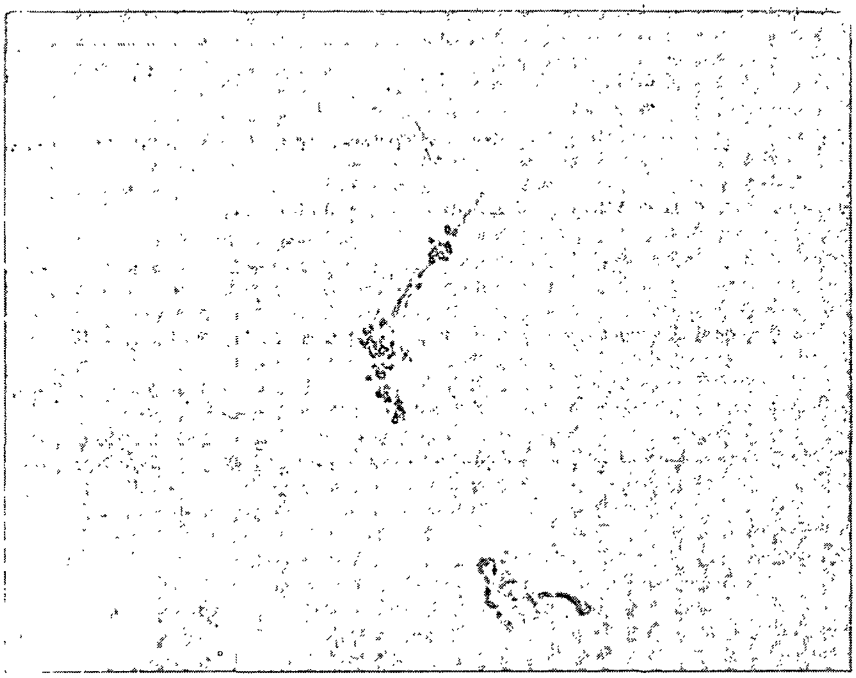

Figure 9. Flocculent Material Formed from Hardwood Groundwood Pitch; Small Amount of Fiber + 100 mg/L of $Al_2(SO_4)_3$ Added at pH 4. 600X

As a further test of colloidal stability, samples of isolated pitch from the beaten kraft and groundwood pulps were subjected to high shear conditions for 20 minutes at room temperature in a Virtis Homogenizer. The effect of shear on particle size distribution was determined in the case of the groundwood pitch with the aid of an image analyzer. The research model microscope and hemacytometer used in the manual counting procedure were utilized in combination with the image analyzer through an optical adaptor. An auxiliary 3.3X lens was used in the trinoc position which brought the effective magnification to approximately 1200X on the image analyzer screen. The oversize count module was used in sizing the particles. Results are recorded in Table IV and the distributions are shown graphically in Fig. 10 and 11.

TABLE IV

PARTICLE SIZE DISTRIBUTION OF GROUNDWOOD PITCH

Particle Size, μm	% of Particles in Given Size Range	
	Before Shearing	After Shearing
0-0.27	17.7	14.2
0.27-0.55	7.7	17.4
0.55-0.82	5.7	11.1
0.82-1.10	21.3	16.8
1.10-1.37	13.4	11.8
1.37-1.64	17.5	10.8
1.64-1.92	3.3	7.6
1.92-2.19	8.9	3.9
2.19-2.74	3.3	2.9
>2.74	1.2	3.4
	402 Particles Counted	378 Particles Counted

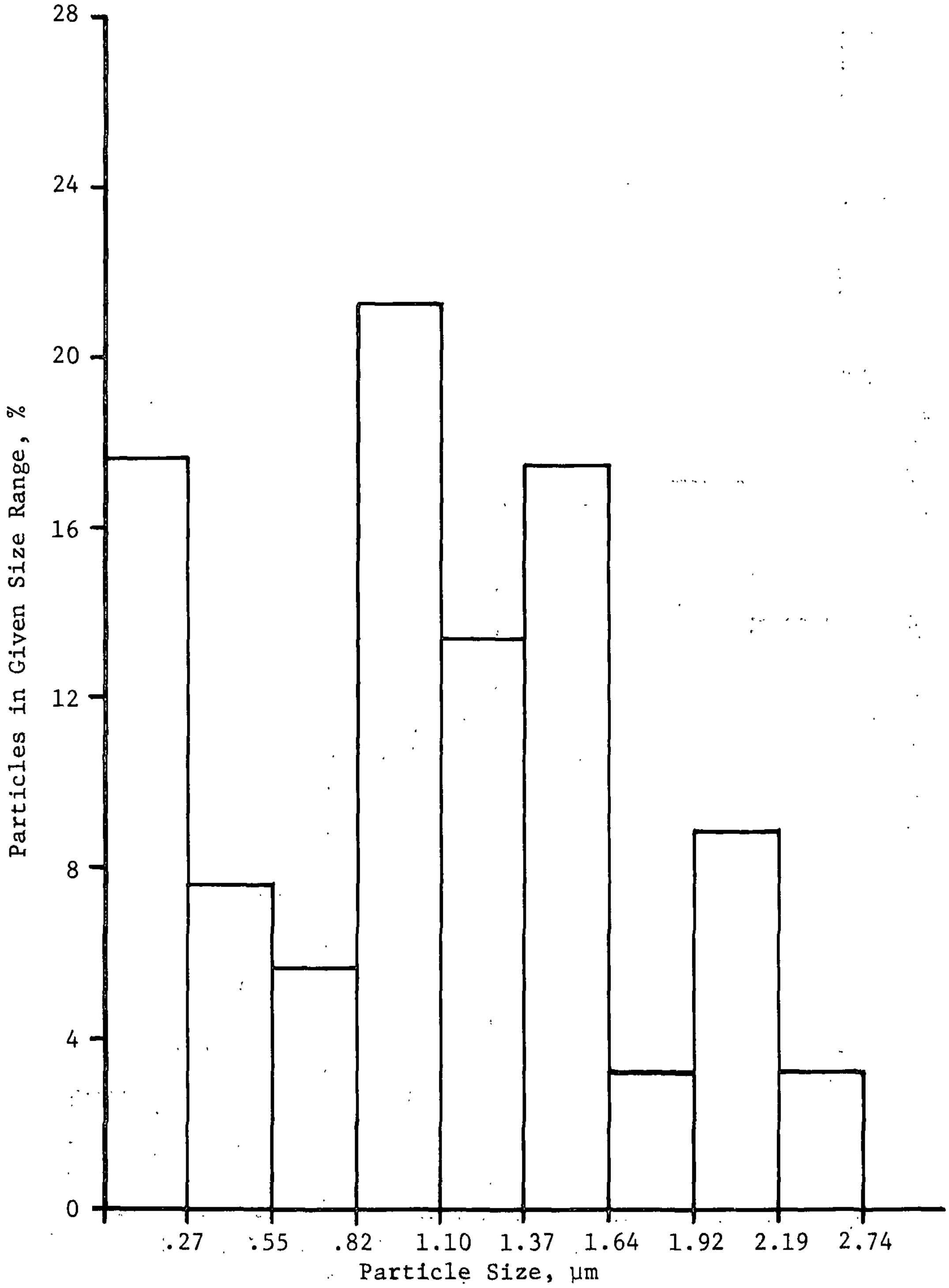

Figure 10. Particle Size Distribution of Groundwood Colloidal Pitch Before Shearing

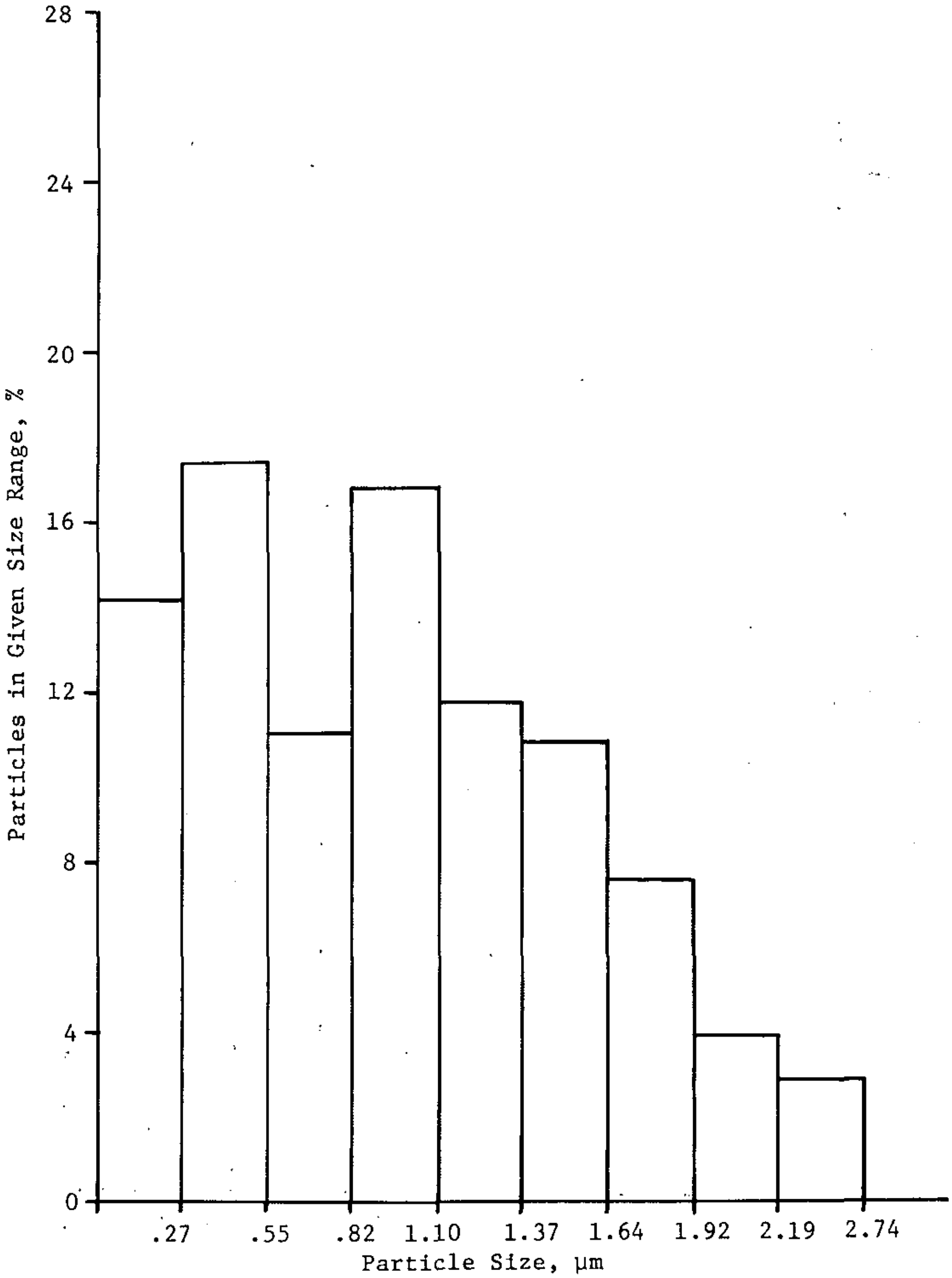

Figure 11. Particle Size Distribution of Groundwood Colloidal Pitch After Shearing

The size of pitch particles isolated from the kraft pulp were quite small and, hence, accurate measurements were not attempted. However, particle counts were made before and after shearing. The particle counts per square in the hemacytometer were 13.9 ± 3.3 before shearing and 13.0 ± 3.08 after shearing. If appreciable agglomeration had occurred with shearing, the number of particles per square would be expected to decrease significantly but such was not the case.

In pursuing colloidal stability studies, 50 mL aliquots of isolated pitch from the kraft, groundwood, and a fresh sample of beaten Mitscherlich sulfite pulp were reduced in volume in a rotoevaporator in the absence of added salts. The pitch suspensions were warmed slightly ($\underline{\sim}$ 100°F) during this operation. Samples were withdrawn periodically and examined under the microscope at 600X using phase contrast. Results are summarized in Table V.

Since little or no reference is made in the literature to matrix flocs containing trapped pitch particles, the decision was made to examine a pulp mill system for similar floc networks. Accordingly, samples were drawn from a kraft mill at several locations extending from the brown stock washers to the paper machine tray water. The pulp samples were pressed to remove water and the filtrates, along with headbox and tray water samples, were examined under the microscope at 600X. Additionally, several filtrates were concentrated in a rotoevaporator and then reexamined. Results are summarized in Table VI. Photomicrographs of flocculent material from the tray water are presented in Fig. 12 and 13.

CHEMICAL ANALYSIS

An analysis was made of colloidal pitch and pitch precipitates formed with addition of aluminum and calcium sulfates. The samples were first concentrated to near dryness at 50°C in a rotoevaporator, then dried overnight and weighed.

TABLE V

THE EFFECT OF CONCENTRATING COLLOIDAL PITCH IN THE ABSENCE OF ADDED SALTS

Source of Colloidal Pitch	Volume at Time of Sampling, mL	Observations
Unbleached kraft (250 mL CSF)	50	Individual pitch particles evident — no evidence of floc formation
	25	Slight evidence of matrix floc formation but most pitch in individual particle form
	17	Considerable evidence of matrix floc with trapped pitch particles — no evidence of agglomerated pitch particles
	5	More evidence of matrix floc with trapped pitch particles — no evidence of agglomerated pitch particles
	1	Same as above with additional large particles of unknown material which apparently precipitated with increase in concentration
Unbleached Mitscherlich sulfite (50 mL CSF)	50	Individual pitch particles evident — no evidence of floc formation
	34	Some evidence of small (<10 μm) matrix flocs — no evidence of agglomerated pitch particles
	15	Increased evidence of small (<10 μm) matrix flocs — no evidence of agglomerated pitch particles
	10	Increased evidence of small (<10 μm) matrix flocs — no evidence of agglomerated pitch particles
Unbleached groundwood	50	Individual pitch particles evident — no evidence of floc formation
	20	Individual pitch particles evident — no evidence of floc formation
	10	Individual pitch particles evident — no evidence of floc formation
	2.5	Matrix floc with trapped pitch particles evident — no evidence of agglomerated pitch particles

TABLE VI

EXPLORATORY EXAMINATION OF KRAFT MILL PULP AND WATER SAMPLES WITH RESPECT TO PITCH AND FLOC FORMATION

Sample Description	pH	Observations
Pulp from brown stock washers	9.3	Sample was pressed to remove water. Filtrate found to contain relatively large number of pitch particles but no flocculent material. Filtrate concentrated with roto evaporator. Starting with 50 mL, volume was reduced stepwise down to 6 mL without evidence of floc formation; however, pitch particles evident — some as large as 5 µm.
Pulp from deckers	8.6	Sample was pressed to remove water — some pitch particles evident, but considerably less than in washer stock. No evidence of flocculent material.
Pulp sampled after refiners	5.1	Very few pitch particles evident. Sample concentrated: 50 mL → 15 mL → 4 mL. Little or no evidence of flocculent material at 4 mL.
Headbox stock	5.1	Large flocs with fines and some spherical particles evident.
Tray water	4.8	Many large flocs present, some over 200 µm in diameter; flocs found to contain a rather low level of spherical particles. pH of sample adjusted to 10 without evidence of physical change.

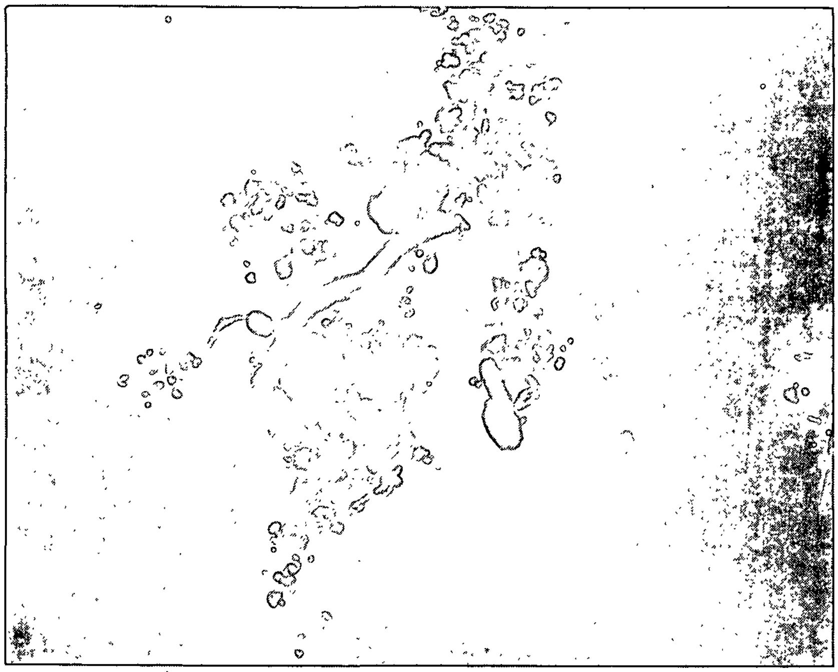

Figure 12. Tray Water Floc — Dark Field Illumination. 150X

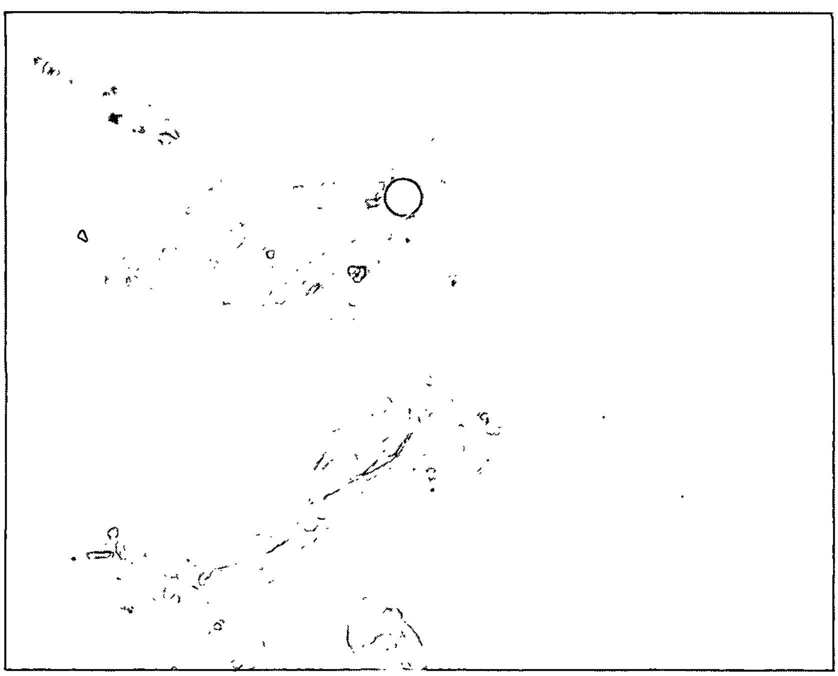

Figure 13. Tray Water Floc — Phase Contrast. 600X

The pitch in each sample was determined by extraction with hot benzene-alcohol (2:1 by volume). Part of the residue from the solvent extractions was used to determine sugars (carbohydrates) by gas-liquid chromatography. The remainder of the residue was ashed and the metal content in the ash was determined by emission spectroscopy. Results of the analyses are recorded in Table VII. Note: Table VII includes an analysis of deposits accumulated in a microdeposit test using kraft pulp and aluminum sulfate. The microdeposit test is described in the next section.

MICRODEPOSIT TESTS

The following general procedure was employed in determining pitch deposit levels by a microdeposit test: Fifty milliliters of isolated pitch suspension with and without aluminum sulfate or calcium sulfate was placed in a 125-mL stainless steel beaker fitted with a plastic cover with centered hole large enough to accommodate the shaft of a Lightnin' stirrer. The stirrer included a three bladed stainless steel propeller having a maximum diameter of about 1-1/4 inches. The propeller was adjusted to clear the bottom of the beaker by about 1/16 inch. The assembly, shown in Fig. 14, was placed in a constant temperature bath at 120°F ($\sim$ 49°C) and stirring was started immediately. The temperature was controlled during the stirring period which was varied from 30 minutes to 2 hours. Agitation rate was controlled with a rheostat and measured with a tachometer. After the specified period, the agitation procedure was stopped and the propeller was rinsed with distilled water and cautiously removed from the stirrer shaft so as not to disturb the material deposited on the blades. The difference in dry weight between the propeller before and after the experiment was determined on a semimicrobalance. In order to determine if the material deposited on the propeller was comprised entirely of pitch, the blades were washed with solvent (2:1 benzene-alcohol),

TABLE VII

COMPOSITION OF COLLOIDAL PITCH AND PITCH PRECIPITATES

Sample No.	Identification - Additives	Solvent Solubles, %	Total Carbohydrate, %	Cellulose/ Hemicellulose Ratio	Ash Content, %	Emission Spec. Analysis (metal content)
1	Colloidal pitch suspension from kraft pulp	--	--	1.22	--	--
2	Kraft colloidal pitch + 100 mg/l $Al_2(SO_4)_3$ at pH 4	21.0	30.0	1.22	23.9	Al 2.8%; Si 1.9%
3	Kraft colloidal pitch + 344 mg/l $CaSO_4 \cdot 2H_2O$, pH 7	17.0	34.2	2.98	44.8	Ca 4.5%; Mg 4.3%
4	Colloidal pitch suspension from groundwood pulp	--	--	2.54	--	--
5	Groundwood colloidal pitch + 100 mg/l $Al_2(SO_4)_3$, pH 4	40.0	39.3	1.44	5.7	Si 1.3; Al 0.74%
6	Composite material collected in microdeposit tests using the kraft pulp and $Al_2(SO_4)_3$	15.0	20.8	.625	32.0	Al 3.1, Si 2.6, Fe 2.6

dried, and reweighed. Results of exploratory tests with the kraft and groundwood pulps are recorded in Table VIII.

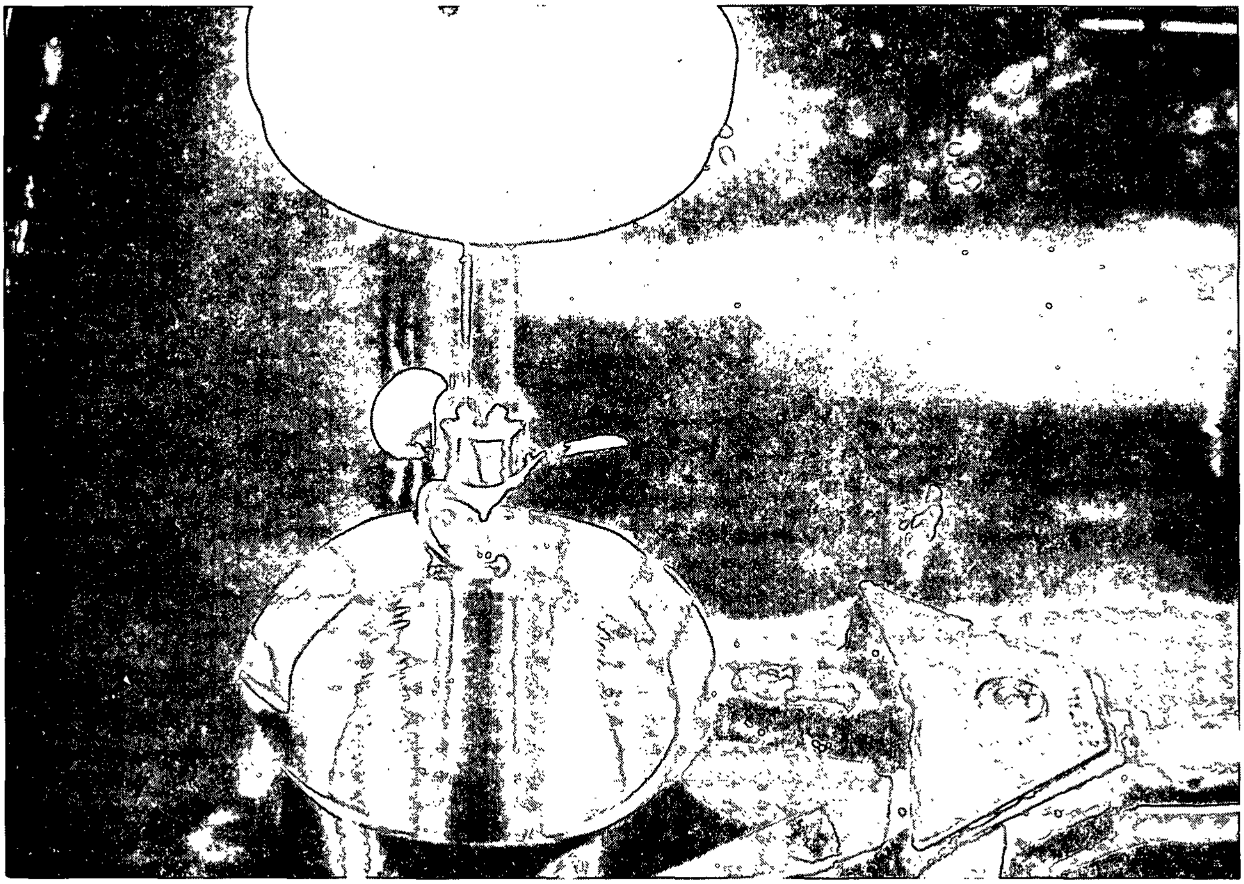

Figure 14. Pitch Microdeposit Device

A subsequent series of deposit tests with the kraft pulp was carried out in which the matrix floc was concentrated and then used to study deposition tendencies as a function of stirring rate, stirring time, temperature, and pH. The effects of a commercial grade of pitch dispersant (sodium naphthalene sulfonate) and fiber content were also examined. In the matrix floc concentration procedure, pitch was isolated in the normal manner then 100 mg/L of aluminum sulfate at pH 4 was added. This material was allowed to stand until completely settled. Seventy-five percent of the total liquid volume was then decanted off and the remaining liquid with floc was used in the test. The effect of adding kraft fiber and a

TABLE VIII

MICRODEPOSIT TEST—PRELIMINARY EXPERIMENTS

Test No.	Pulp	Additives	pH	Deposit Level, Mg. Test 1	Test 2	Av.	Deposit Level, mg After Washing with Solvent
1	Beaten unbl. kraft	None (control)	8.1	.05	.03	.04	.01
2	" " "	$Al_2(SO_4)_3$, 100 mg/l	4.0	.18	.19	.18	.17
3	" " "	" "	5.0	.05	.06	.06	.04
4	" " "	$CaSO_4$, 344 mg/l	7.0	.05	--	--	--
5	Aspen stone groundwood	None (control)	6.4	.03	.07	.05	.04
6	" " "	$Al_2(SO_4)_3$, 100 mg/l	4.0	.27	.28	.28	.17
7	" " "	" "	5.0	.29	.15	.22	.13
8	" " "	$CaSO_4$, 344 mg/l	7.0	.10	.20	.15	.07

dispersant was included in this series. Kraft fiber was added before the addition of alum and the concentration step whereas the dispersant was added to the concentrated pitch suspension. Results are recorded in Table IX.

The concentration of matrix floc was determined by filtering an aliquot of the suspension onto 0.1 µm Millipore paper in which case the filtrate was clear. The concentration of matrix floc in the kraft pulp after concentrating 4X was found to be 0.0136%.

A second series of microdeposit tests was carried out using the groundwood pulp, in which case it was not necessary to concentrate the isolated colloidal pitch since the groundwood pulp contained a higher concentration of pitch particles, i.e., approximately 0.016% in matrix form. This series was limited to the affects of rate of agitation, pH, dispersant level, and fiber content. The time and temperature of agitation were held constant at two hours and 120°F, respectively. Results are presented in Table X. Note: Tables IX and X include zeta potential in a limited number of cases. A Zeta Meter and standard procedures were used in these determinations.

The effects of matrix floc concentration, temperature, and time of agitation on deposit level from the kraft pulp are presented in Fig. 15-17. The effects of rate of agitation, pH, dispersant level, and fiber content on deposit level for both pulps are given in Fig. 18-21. Zeta potential as a function of pH is presented in Fig. 22. Deposit level-zeta potential relationships are presented in Fig. 23.

TABLE IX

MICRODEPOSIT TEST — RESULTS FROM UNBLEACHED KRAFT PULP
(ALUMINUM SULFATE ADDED AT 100 MG/L)

Test No.	Other Additives	pH	Zeta Potential, mv	Matrix Floc Concn.	Temp., °F	Time of Agitation, hr	Rate of Agitation, rpm	Deposit Level, mg Test 1	Test 2	Av.
9	None	8.1	-22.5	Control[a]	120	2	2700	0.05	0.03	0.04
10	None	4.0	--	Normal	120	2	2700	0.18	0.19	0.18
11	None	4.0	-3.5	4X	120	2	2700	0.41	0.44	0.42
12	None	4.0	--	4X	100	2	2700	0.32	0.31	0.32
13	None	4.0	--	4X	80	2	2700	0.30	0.21	0.26
14	None	4.0	--	4X	120	1	2700	0.22	0.22	0.22
15	None	4.0	--	4X	120	1/2	2700	0.13	0.20	0.16
16	None	4.0	--	4X	120	2	3600	0.73	0.56	0.64
17	None	4.0	--	4X	120	2	2100	0.17	0.18	0.18
18	None	5.0	+8.3	4X	120	2	2700	0.05	0.06	0.06
19	None	8.0	-9.3	4X	120	2	2700	0.04	0.01	0.02
20	None	10.0	--	4X	120	2	2700	0.04	0.03	0.04
21	Sod. naphthalene sulf.,[b] 25 mg/L	4.0	--	4X	120	2	2700	0.16	0.16	0.16
22	Sod. naphthalene sulf., 50 mg/L	4.0	--	4X	120	2	2700	0.05	0.05	0.05
23	Sod. naphthalene sulf., 100 mg/L	4.0	--	4X	120	2	2700	0.07	0.05	0.06
24	Sod. naphthalene sulf., 50 mg/L	5.0	--	4X	120	2	2700	0.02	0.05	0.04
25	Fiber, 0.01%	4.0	--	4X	120	2	2700	0.64[c]	0.68[c]	0.66[c]
26	Fiber, 0.025%	4.0	--	4X	120	2	2700	0.17[c]	0.12[c]	0.14[c]
27	Fiber, 0.05%	4.0	--	4X	120	2	2700	0.05[c]	0.05[c]	0.05[c]
28	Whole pulp (no additives)	8.8	--	As is	120	2	2700	0.05[c]	0.09[c]	0.07[c]
29	Whole pulp (alum added)	4.0	--	4X	120	2	2700	0.04	0.02	0.03

[a] No aluminum sulfate added.
[b] Sodium naphthalene sulfonate.
[c] Considerable amount of fiber evident in these deposits.

TABLE X

MICRODEPOSIT TEST—ASPEN STONE GROUNDWOOD
(ALUMINUM SULFATE ADDED AT 100 MG/L)

Test No.	Other Additives	pH	Zeta Potential, mv	Temp., °F	Time of Agitation, hr	Rate of Agitation, rpm	Deposit Level, mg Test Values	Deposit Level, mg Av.
30	None	4	--	120	2	1350	.05, .06	.06
31	None		-9.1			1800	.34, .40, .25, .34, .27, .41, .39	.34 ± .06
32	None		--			2100	.19, .29, .18, .48, .25, .24, .50, .22, .23	.29 ± .11
33	None		--			2700	.13, .10, .16	.13 ± .03
34	None		--			3600	.08, .05	.06
35	None	5	+4.7	120	2	1800	.09, .12	.11
36	None	8	+8.0	120	2	1800	.97, .53	.75
37	None	10	-7.6	120	2	1800	.04, .03	.04
38	Sodium naphthalene sulfonate, 25 ppm	4	--	120	2	1800	.06, .09	.08
39	Sodium naphthalene sulfonate, 50 ppm	4	--	120	2	1800	.03, .04	.04
40	Sodium naphthalene sulfonate, 100 ppm	4	--	120	2	1800	.03, .03	.03
41	Sodium naphthalene sulfonate, 25 ppm	8	--	120	2	1800	.16, .44, .16	.25 ± .16
42	Sodium naphthalene sulfonate, 50 ppm	8	--	120	2	1800	.09, .11	.10
43	Sodium naphthalene sulfonate, 100 ppm	8	--	120	2	1800	.07, .08	.08
44	Fiber, 0.01%[a]	4	--	120	2	1800	.28, .16	.22
45	Fiber, 0.025%[a]	4	--	120	2	1800	.25, .38	.32
46	Fiber, 0.05%[a]	4	--	120	2	1800	.19, .15	.17
47	Fiber, 0.10%[a]	4	--	120	2	1800	.31, .39	.35

[a]Fiber concentration.

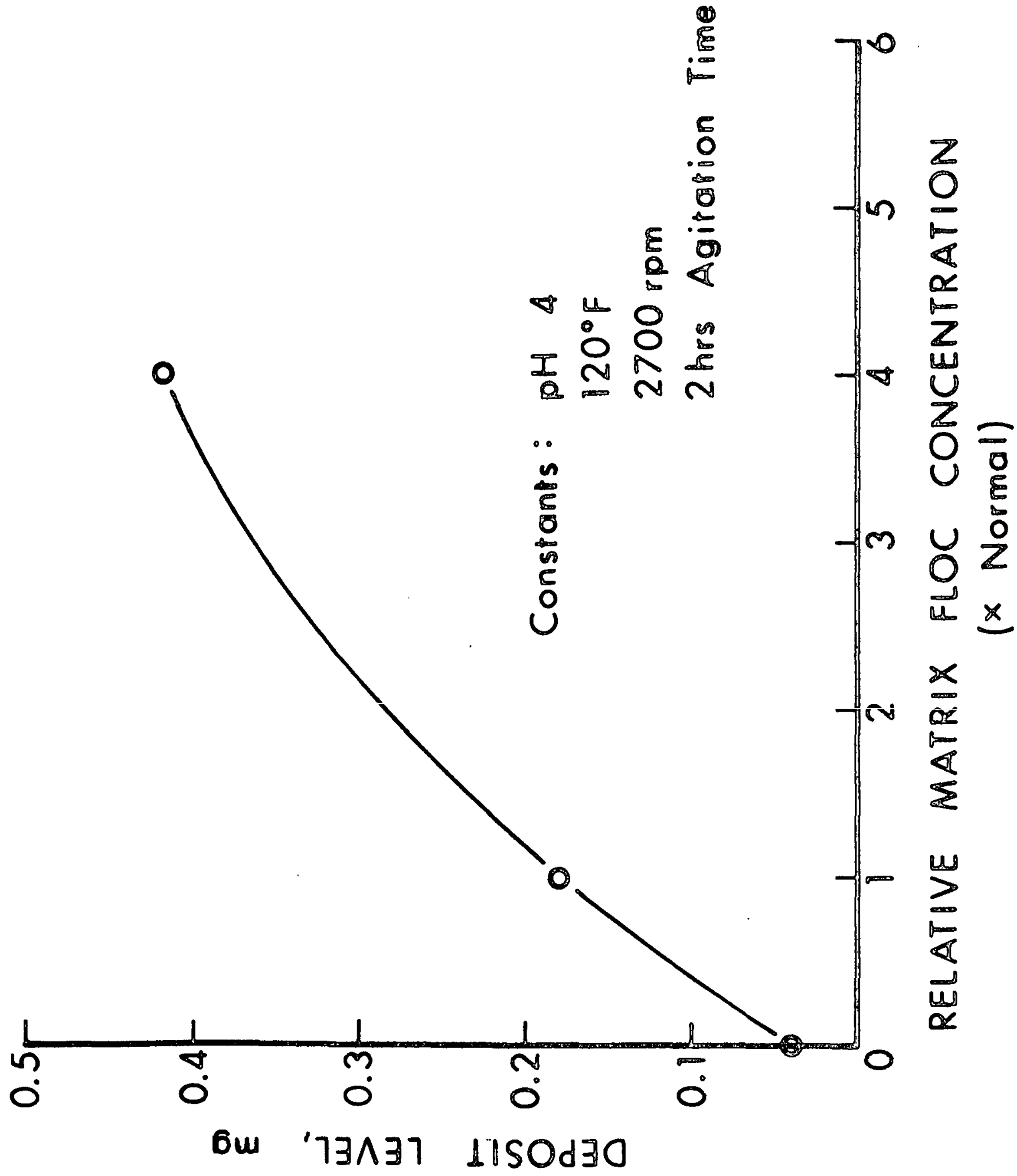

Figure 15. The Effect of Matrix Floc Concentration on Deposit Level for Kraft Pulp with 100 mg/L $Al_2(SO_4)_3$

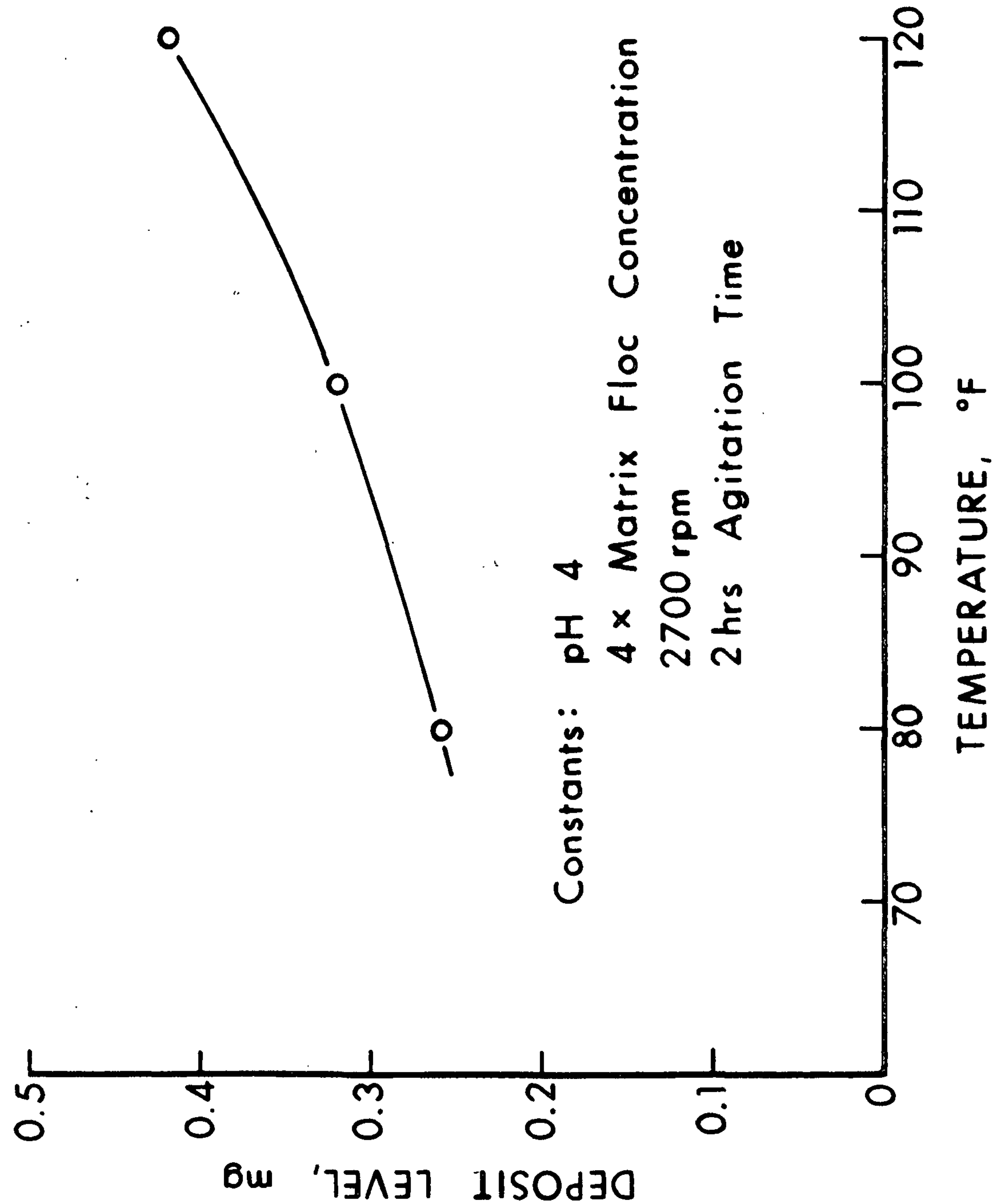

Figure 16. The Effect of Temperature on Deposit Level for Kraft Pulp with 100 mg/L $Al_2(SO_4)_3$

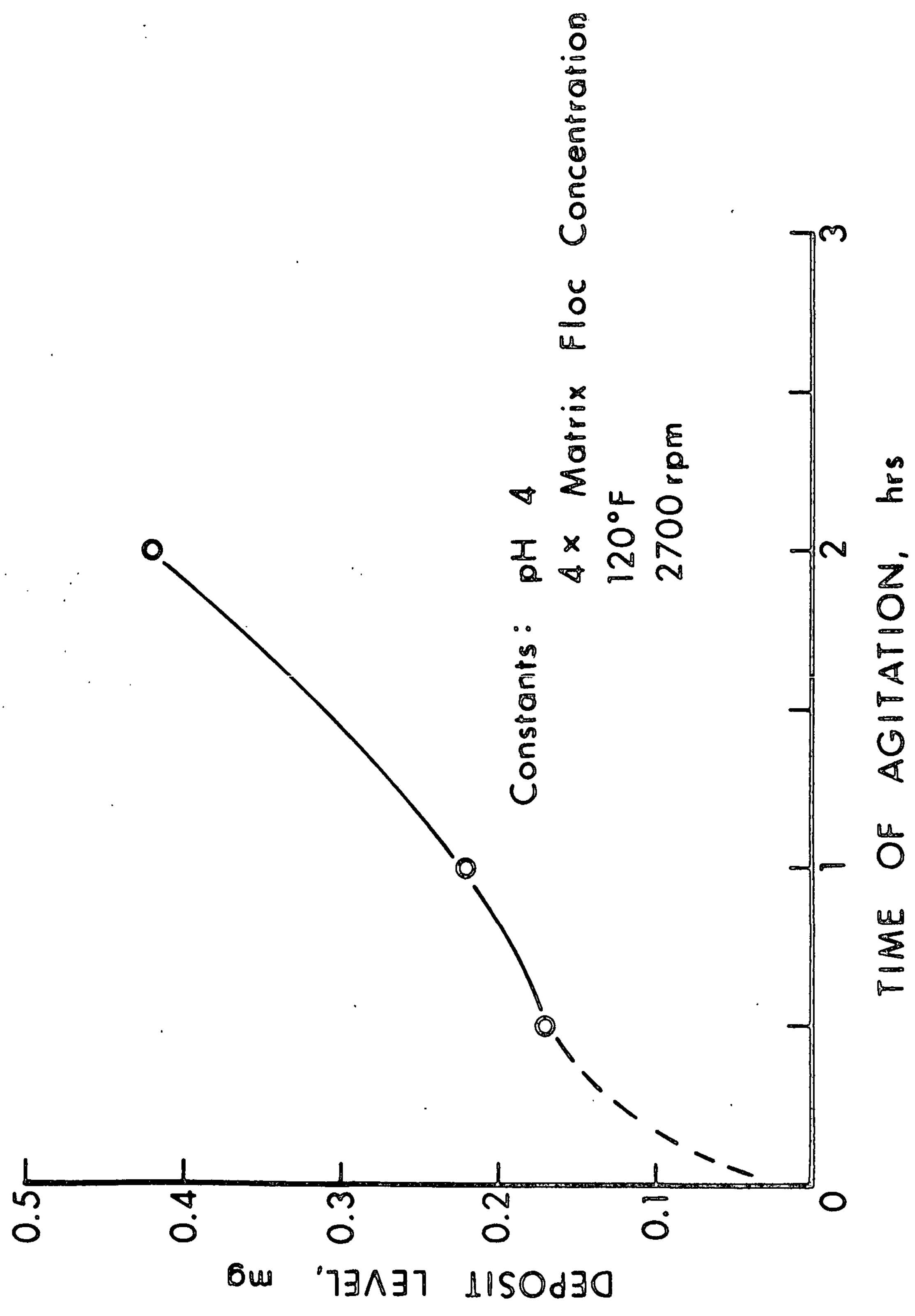

Figure 17. The Effect of Agitation Time on Deposit Level for Kraft Pulp with 100 mg/L $Al_2(SO_4)_3$

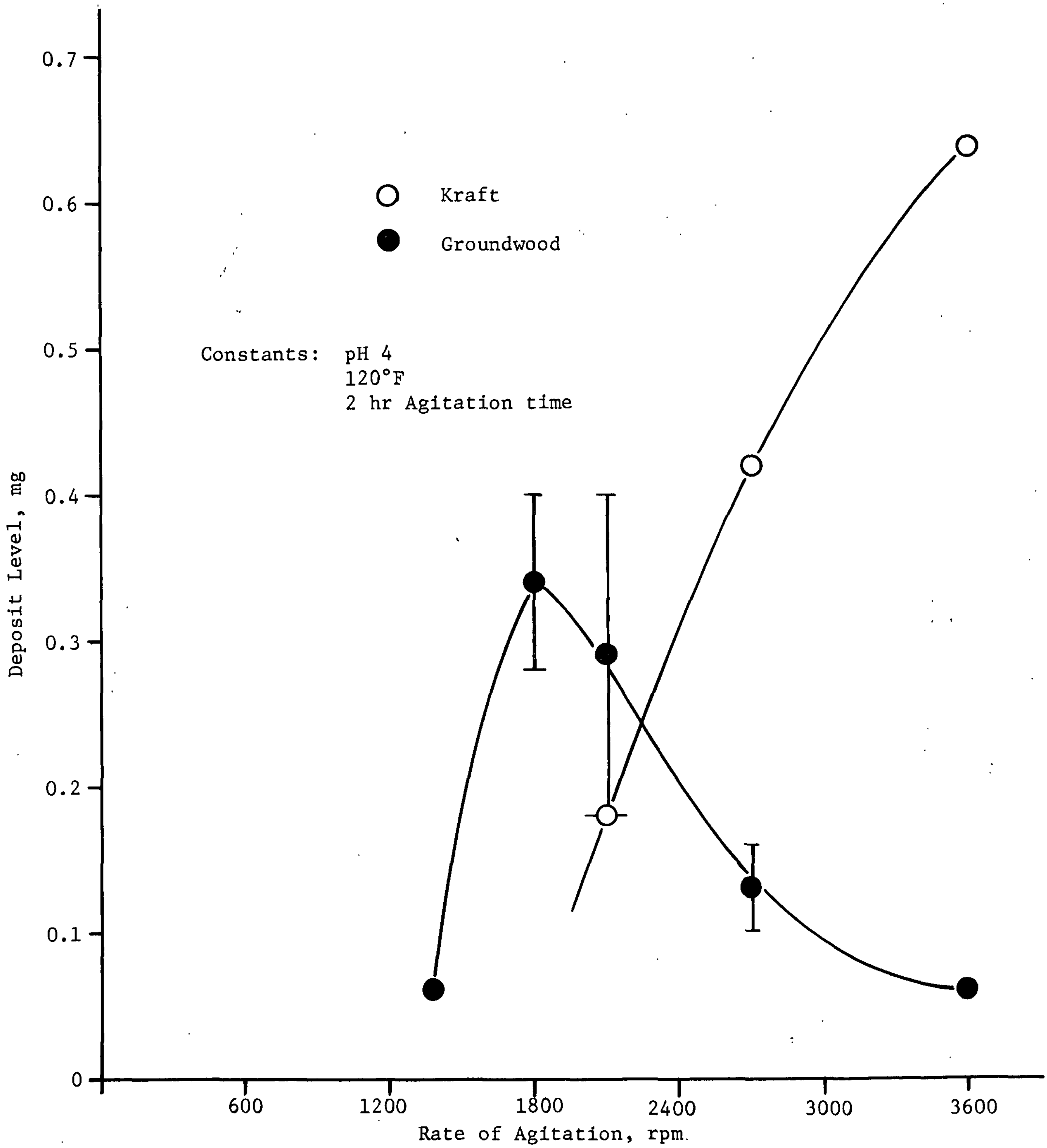

Figure 18. The Effect of Agitation Rate on Deposit Level in Presence of 100 mg/L of $Al_2(SO_4)_3$

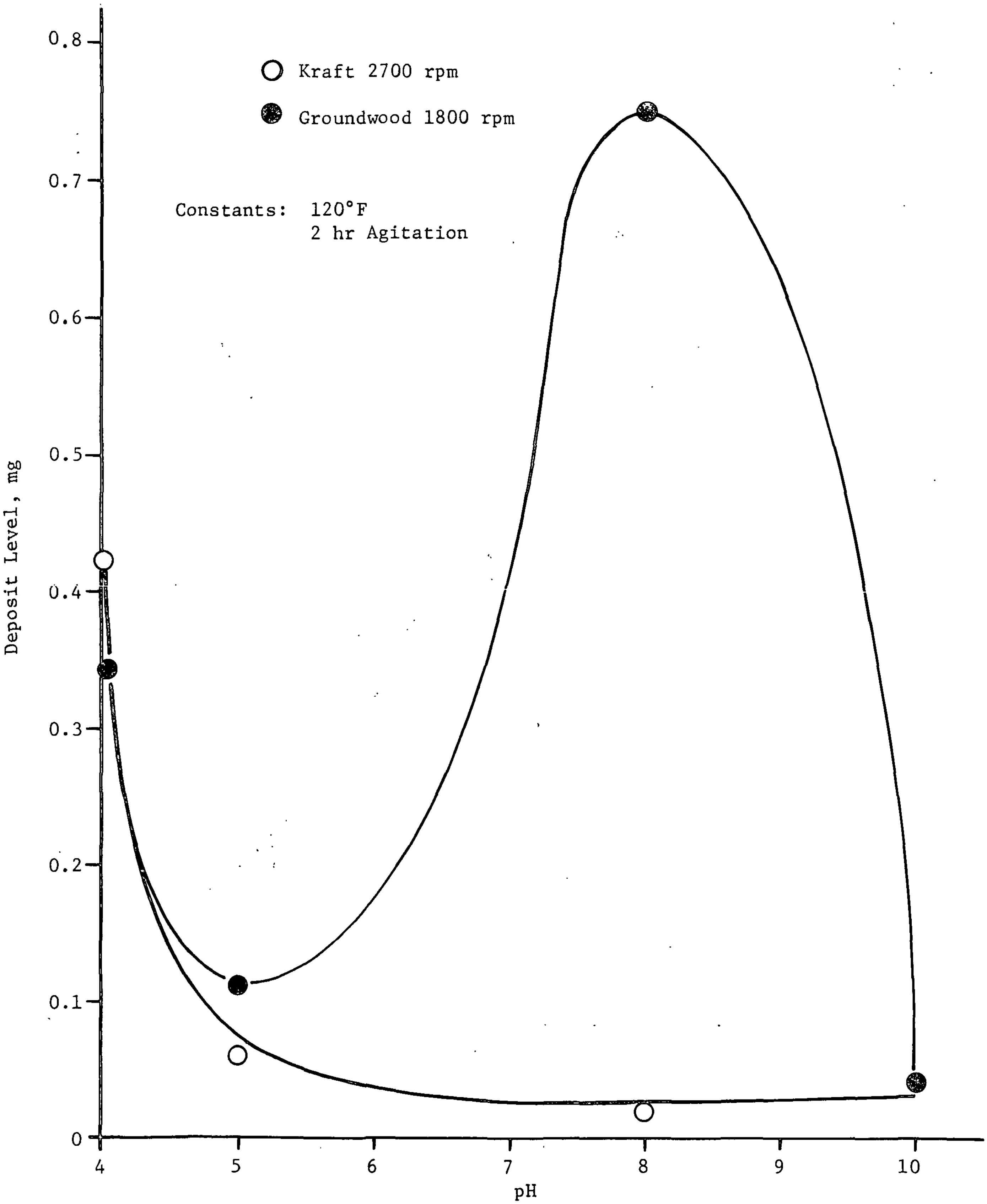

Figure 19. The Effect of pH on Deposit Level in Presence of 100 mg/L of $Al_2(SO_4)_3$

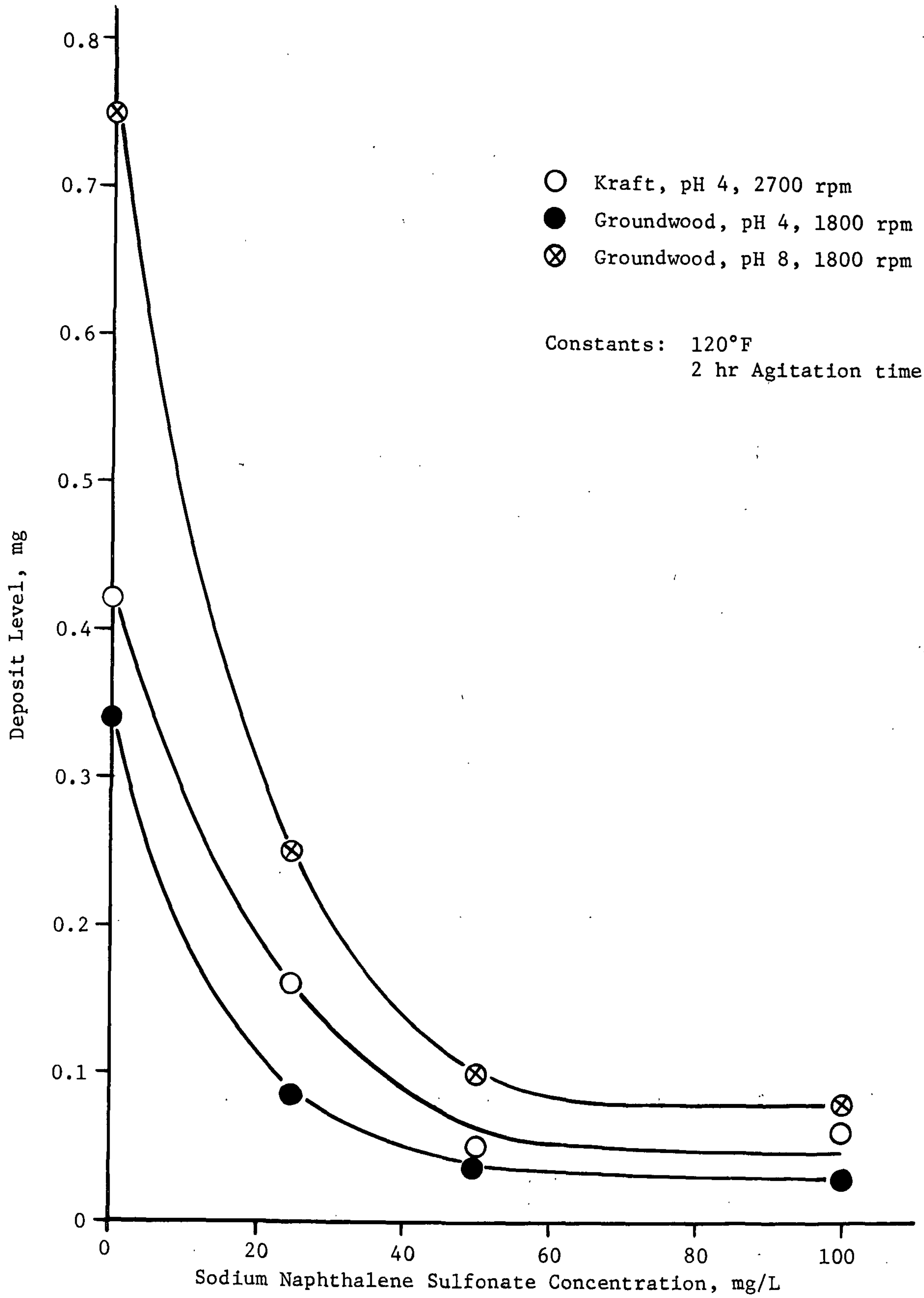

Figure 20. The Effect of Dispersant on Deposit Level in Presence of 100 mg/L of $Al_2(SO_4)_3$

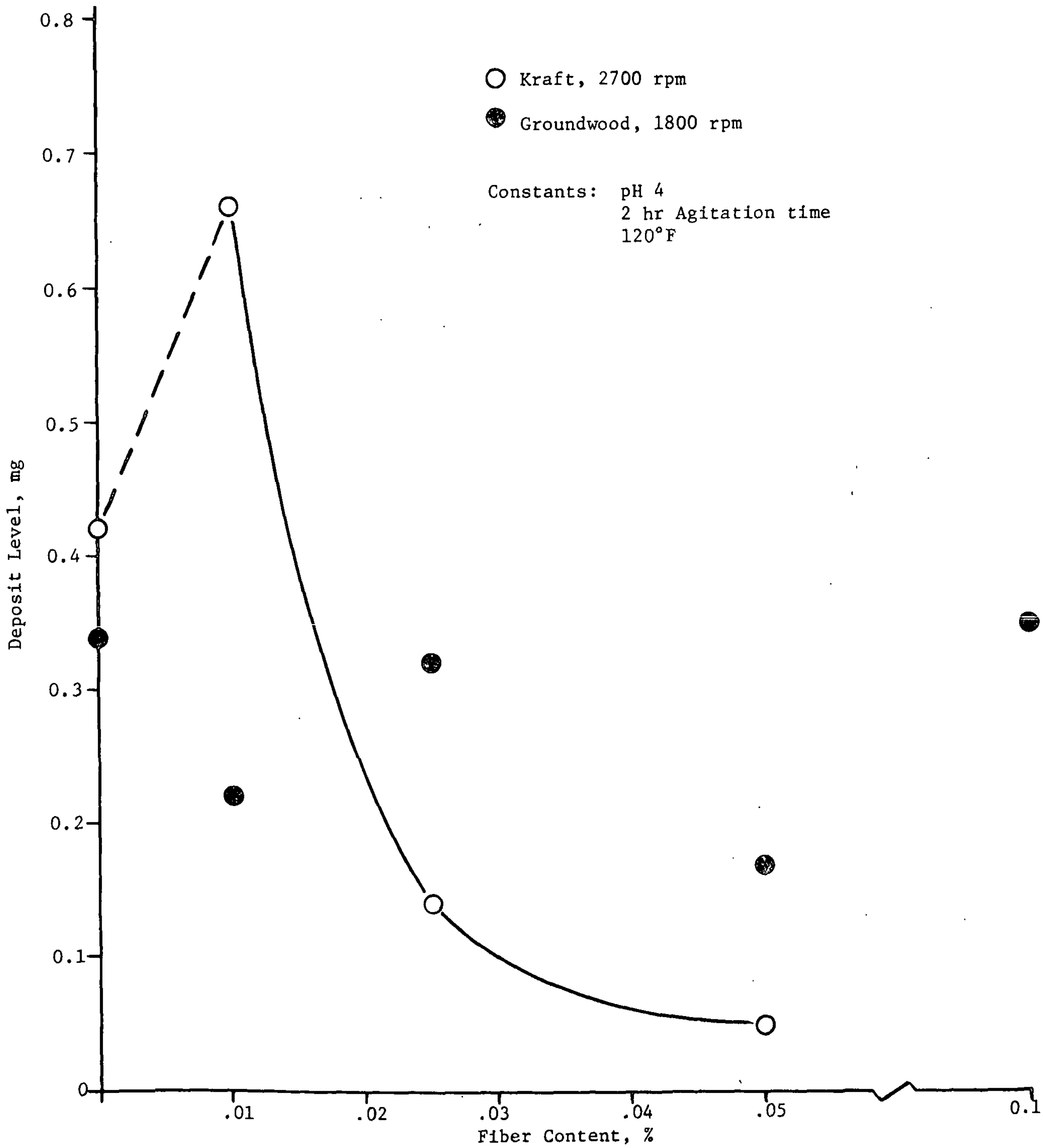

Figure 21. The Effect of Fiber Content on Deposit Level in the Presence of 100 mg/L of $Al_2(SO_4)_3$

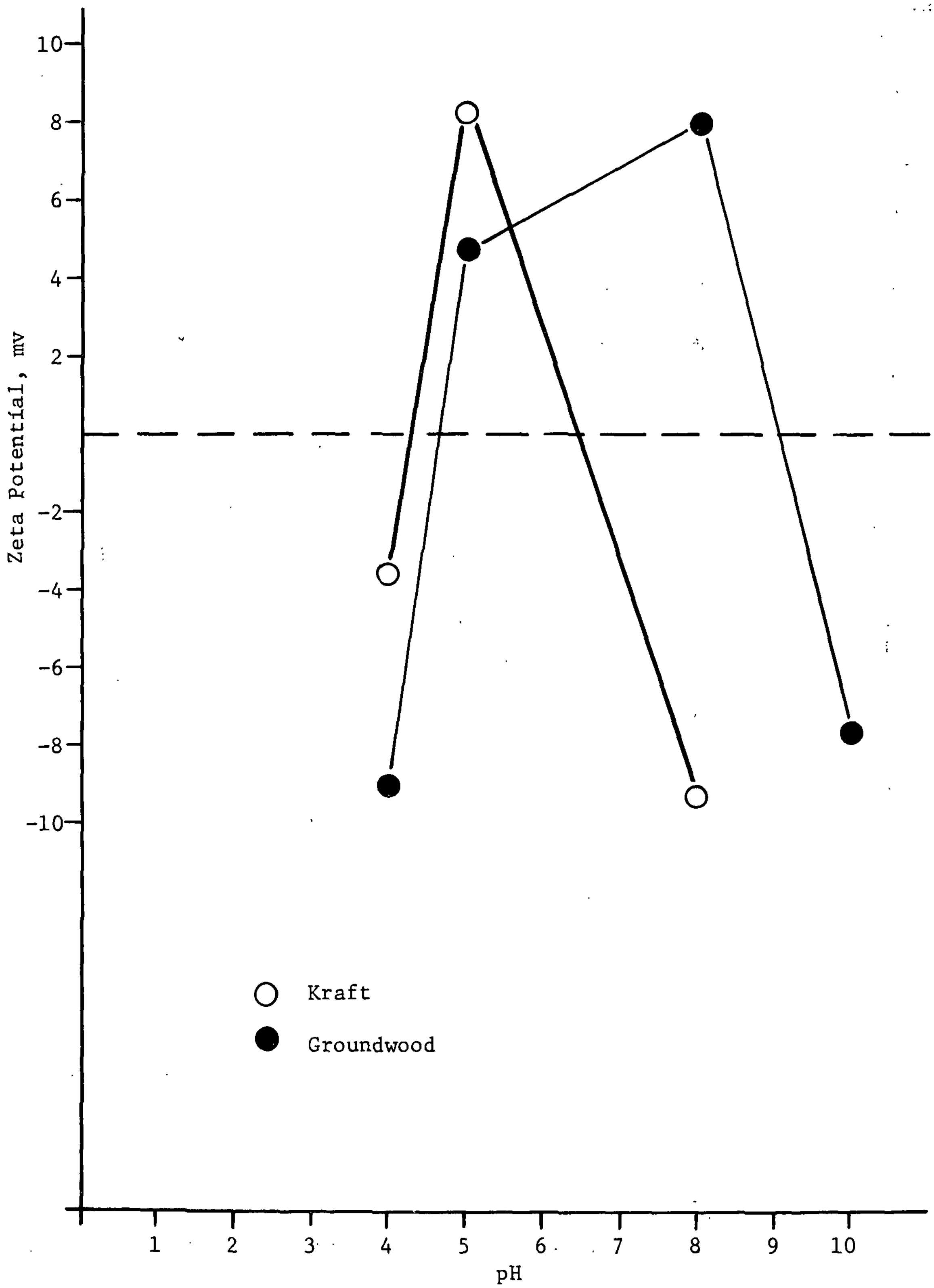

Figure 22. The Effect of pH on Zeta Potential in the Presence of 100 mg/L of $Al_2(SO_4)_3$

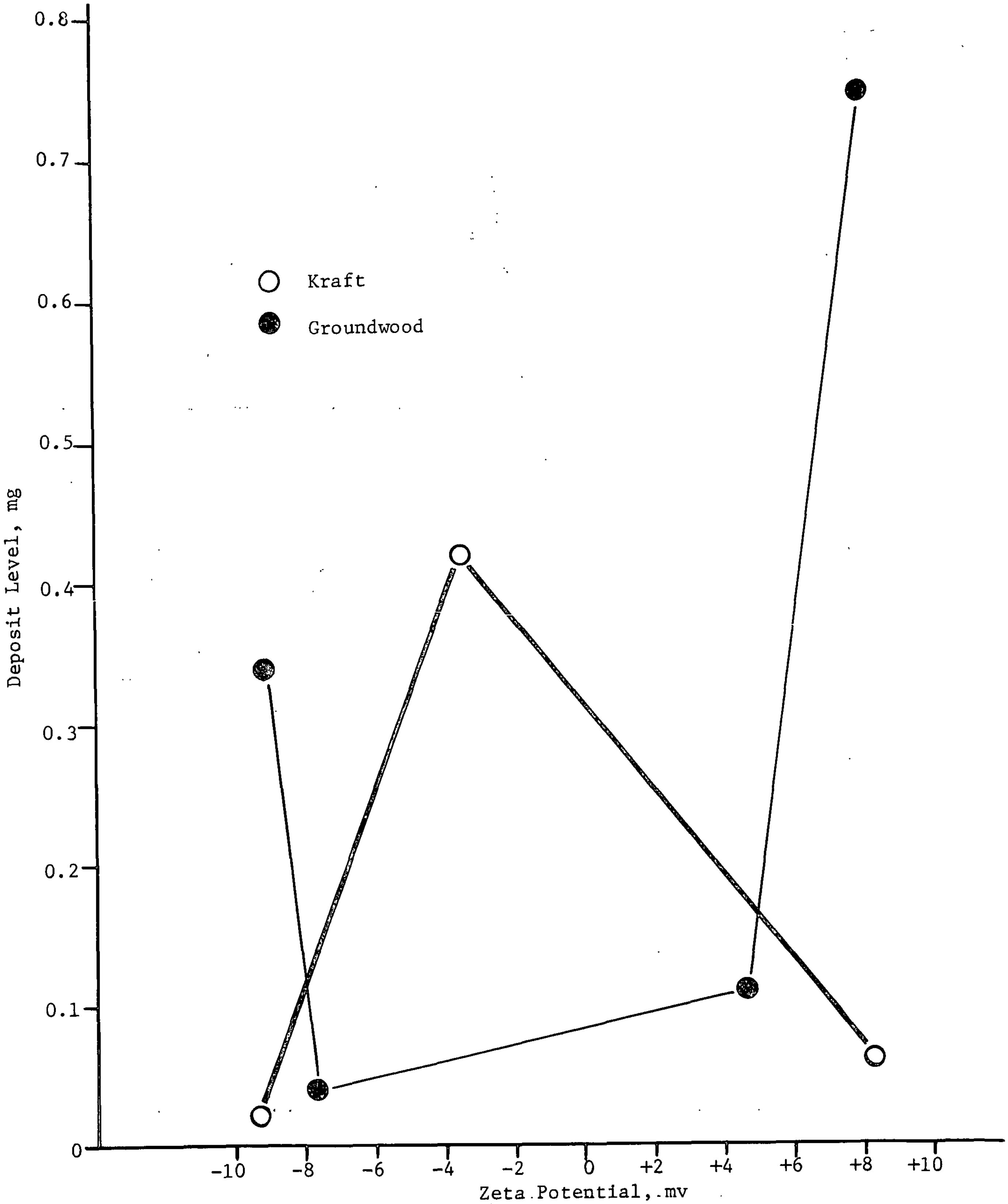

Figure 23. Deposit Level as a Function of Zeta Potential in the Presence of 100 mg/L of $Al_2(SO_4)_3$

DISCUSSION OF RESULTS

A substantial difference in particle count is indicated in Table I between the groundwood and kraft pulps while the actual deposit levels were quite comparable. Contrary to what might be expected on the basis of these results, the groundwood pulp was not considered particularly bothersome in mill operations whereas the kraft pulp was said to cause deposits on the paper machine. The problem with the kraft pulp was attributed to the presence of balsam fir since little or no difficulty is normally experienced when this species is removed from the wood supply. Of the particles counted, 61-86% were considered to be pitch and, since the unbeaten kraft contained a rather low colloidal particle concentration, the decision was made to use beaten kraft in all subsequent studies.

Regression analysis of the data in Table II indicates a half-life in excess of 10 years for the groundwood pitch suspension and 1-2 months for the kraft pitch. The resulting particle count-time relationships are presented in Fig. 1 which includes the previously tested Mitscherlich sulfite pitch for purposes of comparison.

Matrix-type floc networks developed when the isolated pitch was either concentrated or treated with 100 mg/L of aluminum sulfate at pH 4 or 344 mg/L of calcium sulfate at pH 7. In the presence of aluminum and calcium ion, smaller, less distinct flocs were encountered in the groundwood pitch than those found in the kraft and previously tested sulfite pitch. Further, somewhat more time was required for floc development in the groundwood pitch (Table III). Some flocs formed from groundwood pitch in the presence of calcium ion were small enough to be of colloidal size. Nevertheless the ability of the floc network to trap and immobilize pitch particles is confirmed in Table III and Fig. 2-9. The greater rate of destabilization of pitch from the kraft pulp is confirmed in Fig. 2 and 3. Figures 5, 7, and 9 show that fibers and fines become attached to the matrix flocs in the presence of aluminum and calcium sulfate as used in these experiments. In some cases fines and fiber fragments appear to be imbedded in the flocs.

The particle size data in Table IV and Fig. 10 and 11 are quite erratic but there is no evidence of a shift to larger particle sizes as would be expected if agglomeration had occurred as a result of shearing. Results previously reported for sulfite pitch showed similar behavior. Likewise, particle counts made on kraft pitch before and after shearing remained essentially constant indicating that a significant change in particle size had not occurred. Presumably the presence of protective colloids prevented agglomeration under high-shear conditions.

Results in Table V indicate that matrix-type floc networks form in the absence of added salts. If it is permitted to extend the results in Table V to practical paper machine conditions, matrix flocs from the kraft and sulfite pulps were formed at a fiber consistency equivalent to 6-12% or, in effect, at consistencies corresponding to those at the wire section. Matrix flocs from groundwood formed at a significantly higher equivalent consistency corresponding to the drier section. It is recognized, of course, that these results do not consider the rate at which floc formation occurs. However, it is conceivable that, as the concentration increases, the bulky floc networks become attached to one another forming larger flocs. Under these conditions, the flocs could result in wire and felt plugging in spite of the fact that only part of the floc is pitch. The amount and distribution of pitch in addition to its chemical composition would be expected to contribute to the stickiness or tack of the combined floc network.

Examination of samples drawn from a kraft mill system (Table VI) indicates a notable decrease in colloidal pitch particles between the brown stock washers and the deckers as might be expected of an effective washing process. Earlier work with pulp from the same mill also showed a low concentration of colloidal pitch in the decker stock (Table I). Flocculent material containing some pitch particles was found in the headbox and tray water samples. Since rosin size and alum were present at these sampling points, the possibility existed that the flocculent material was hydrated aluminum. However, adjusting the pH of the tray water sample to 10 failed to dissolve or otherwise alter the floc suggesting that it was comprised of some other material, presumably cellulose and/or hemicellulose which was destabilized in the presence of aluminum ion. Comparison of Fig. 5 with Fig. 12 and 13 reveals similar flocculent structures containing a relatively low concentration of pitch particles. Hence, matrixlike flocs produced in the laboratory did not differ substantially in appearance from those found in the paper mill system.

Analysis of colloidal pitch (Table VII) shows that the total carbohydrate content of matrix flocs from the kraft and groundwood pulps remained relatively constant as did the cellulose:hemicellulose ratio in the presence of aluminum sulfate. However, ash and metal contents varied considerably between samples treated in the same manner as in Numbers 2 and 5. It would appear that the matrix formed from kraft pitch retains more aluminum. When compared to pitch from the unbleached sulfite pulp (Report One), the groundwood pitch shows higher solvent solubles and both the kraft and groundwood pitch tended to have higher total carbohydrate contents but lower cellulose:hemicellulose ratios. This was not expected since Mitscherlich sulfite pulp usually contains a high level of hemicellulose.

Exploratory work with the microdeposit test (Table VIII) revealed several noteworthy effects. Perhaps the most significant of these is that only part of the material deposited was pitch as evidenced by the amount left after washing with solvent. It is quite possible, of course, that some pitch was deeply imbedded in the deposit and was inaccessible to the solvent. Nonetheless, where solvent washing was carried out, more than one-half of the deposit remained on the propeller in most cases. A composite of deposits collected when using kraft pulp and aluminum sulfate was shown to contain solvent solubles, carbohydrate, and metals as was found in the suspended flocs (compare Samples 2 and 6 in Table VII). It is interesting to note, however, that while the overall composition of these samples was similar, the deposited pitch differed in the percentages of the individual components. Hence, it appears that matrix flocs deposit on metal surfaces but not necessarily with the original composition.

The groundwood pulp was previously shown to contain a notably higher particle concentration compared to the kraft pulp such that higher deposit levels might be expected as indicated in Table VIII. It may be noted that nonpitchy deposits were found in both the kraft and groundwood controls (Tests 1 and 5) in spite of the fact that no salts were added and matrix-type flocs were absent.

Results in Tables IX and X and Fig. 15-21 reveal several differences in the deposition properties of matrix pitch from the kraft and groundwood pulps. Deposit levels in the case of kraft pitch increased with increase in floc concentration, temperature, and time and rate of agitation. Deposit levels declined with increase in pH, addition of dispersant (sodium naphthalene sulfonate), and addition of fiber. The scope of testing with groundwood pitch was intentionally limited to the effects of rate of agitation, pH, dispersant level, and fiber content. In agreement with kraft pitch, the deposit level from groundwood matrix pitch declined with increase in dispersing agent (Fig. 20). In contrast to kraft pitch, deposit levels from groundwood showed a maximum at pH 8 and 1800 rpm (Fig.

18 and 19). Also, groundwood pitch shows irregular deposition behavior as a function of fiber content whereas kraft pitch deposits declined with increase in fiber content (Fig. 21).

The zeta potential of matrix pitch from the kraft and groundwood pulps was found to be pH dependent in the pH range of 4-10 (Fig. 22). In effect, zeta potential passed from negative values at low pH to positive values at intermediate pH levels followed by a return to negative values at high pH. However, a consistent relationship was not found between deposit level and zeta potential (Fig. 23). Mention should be made that zeta potentials for the previously tested sulfite pitch remained negative in the pH range of 4-7.

Results obtained in the microdeposit tests are in agreement with results reported in the literature in some cases but not in others. In making such comparisons, however, it should be borne in mind that the experimental conditions were not generally comparable. Kahila (2) and Allen (1) report that pitch deposition tends to increase with increase in dispersible pitch content but no reference is made of pitch in matrix floc form. Kahila also indicates that neither the amount of dispersible pitch nor the amount of depositable pitch in unbleached sulfite pulp is dependent upon the amount of solvent extractables.

Gustafsson (3) shows that deposition on stainless steel at 50°C (122°F) increased markedly as the pH increased from 6.0 to 8.0 in unbleached sulfite pulp. In contrast, the deposit level decreased over the same pH range at 5°C. At pH levels of 5.0 and 6.0, pitch deposition on stainless steel reached a maximum at about 10°C followed by a substantial decline as the temperature increased to 40°C. In effect, the temperature at which maximum deposit occurred increased as the pH increased from 5 to 8. Back (4) shows that pitch accumulation on copper propellers reached a maximum at 1000 rpm when stirring a sulfite pulp for 1.5, 3.0, and 4.5 hours. Actually the pitch deposited per unit of time decreased from a rapidly achieved maximum to a very low value. An increase in the temperature of the system lowered the viscosity of the resinous material which favored flow of the resin along and off a smooth deposition surface. In performing deposition experiments with whole pitch or its fractions, Vincent (5) found that deposition reached a maximum at 15°C followed by a dramatic decline at higher temperatures. Vincent also found that deposition increased with increase in pitch concentration and time of agitation.

The effects of aluminum sulfate and dispersing agents on pitch deposition were examined by Gustafsson (3). Pitch deposition from a spruce sulfite pulp was found to reach a maximum at pH 5 with addition of 50 mg/L of aluminum sulfate whereas the deposit level decreased as the aluminum salt was added in amounts up to 150 mg/L at pH 7. Sodium naphthalene sulfonate was found to reduce pitch deposits in the presence of calcium ion most effectively at pH 7.

Of the two pulps examined in this phase of the program it would appear that the groundwood matrix pitch more closely parallels pitch deposition behavior described in the literature. This is based on the differences in deposit level as a function of pH and rate of agitation. The fact that deposit level from kraft pitch increased at agitation rates in excess of 1800 rpm while groundwood pitch declined, may reflect differences in viscosity or fluidity or it may reflect differences in floc size. In general, much of the free acid and combined acid components of pitch are removed in the kraft pulping and washing operations. This leaves a relatively high level of unsaponifiables which melt at higher temperatures than most of the free and combined acid. This could lead to increased deposit levels at higher temperatures.

In review, colloidal pitch isolated from softwood unbleached kraft and hardwood unbleached groundwood pulps has been found to respond to the presence of aluminum and calcium sulfates in much the same manner as was found with Mitscherlich unbleached sulfite pulp as described in Report One. In the absence of added cations, the colloidal pitch was found to be stable with respect to time. Addition of aluminum sulfate at pH 4.0 and calcium sulfate at pH 7.0 resulted in the formation of a matrix-type floc network which trapped individual pitch particles thereby greatly reducing the number of free particles in suspension. Matrix flocs were also found to develop in the absence of added salts when the isolated pitch was concentrated at a slightly elevated temperature. There is also some evidence to suggest that matrixlike flocs are present in practical pulp and paper mill systems. Subjection of isolated pitch to high shear failed to produce any evidence of agglomeration. Microdeposit tests indicated that isolated pitch from the kraft and groundwood pulps differed in their response to changes in pH, agitation rate, and addition of fiber due possibly to differences in the viscosity or fluidity of the pitch or the floc size.

Analyses of colloidal pitch in matrix form revealed that the total carbohydrate content remained reasonably constant while ash and metal content varied considerably as would be expected depending upon the ionic environment. Deposited pitch from kraft pulp was found to contain the same components as the suspended pitch but with some differences in the percentage of individual components.

In considering the results obtained overall in this study of colloidal pitch stability, no evidence has been found to support the hypothesis that individual pitch particles agglomerate to form larger particles, eventually taking the form of pitch balls. This does not rule out the possibility that pitch particles agglomerate in the absence of protective colloids but the preponderance of evidence accumulated under this program suggests that individual pitch particles become trapped or immobilized in matrix flocs. The continuous phase of the floc system is comprised of cellulose, hemicellulose, and possibly some lignin although the presence of lignin has not been established. Trapped individual pitch particles form the discontinuous part of the matrix. Microdeposition data suggest that the entire matrix or a major portion of it deposits on stainless steel surfaces, not merely the pitch component. It appears that flocs of this type also exist in paper mill systems. It is proposed that the bulky matrix flocs with attached fibers and fiber elements agglomerate into larger flocs capable of plugging wires and felts. The amount, distribution, and composition of pitch in the flocs would be expected to determine its tackiness. This hypothesis finds support in the fact that pulp and paper mill deposits are rarely composed solely of pitch but most generally contain fiber elements, gelatinous material and inorganic components.

FUTURE WORK

Emphasis in the experimental program has now shifted to the depositability of pitch in relation to its tackiness and chemical composition. Exploratory work concerned with suitable means of measuring the tackiness of pitch is in progress. In the absence of satisfactory amounts of natural pitch for tack tests and chemical analysis, the decision has been tentatively made to use synthetic pitch comprised of the same components as natural pitch. Analysis of pitch extracted from kraft, sulfite, and groundwood pulps will serve as the basis for formulating synthetic pitch. Formulations of controlled composition will be rated for relative tack and then added in emulsified form to a reference pulp to test depositability. Additionally, it is planned to initiate flotation studies with pitchy pulps and determine the composition of surface films as a function of pH. Hopefully, results derived from the study will identify the troublesome components of pitch and lead to a means of controlling or, preferably, eliminating the problem.

ACKNOWLEDGMENTS

The authors are indebted to Mr. Leroy Borchardt for the analysis of matrix flocs.

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